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Methylene Blue Dye Removal from Aqueous Media Using Activated Carbon Prepared by Lotus Leaves: Kinetic, Equilibrium and Thermodynamic Study

Roya Salahshour, 1 Mehdi Shanbedi 1 and Hossein Esmaeili 2,*

¹ Department of Chemical Engineering, School of Chemical Engineering, Kherad Institute of Higher Education, Bushehr, Iran

² Department of Chemical Engineering, Bushehr Branch, Islamic Azad University, Bushehr, Iran

* Corresponding author: E-mail: esmaeili.hossein@gmail.com esmaeili.hossein@iaubushehr.ac.ir

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Abstract

In the present work, methylene blue was eliminated from aqueous solution using activated carbon prepared by lotus leaves. To perform the experiments, batch method was applied. Also, several analyses such as SEM, FTIR, EDAX and BET were done to determine the surface properties of the activated carbon. The results showed that the maximum sorption efficiency of 97.59% was obtained in initial dye concentration of 10 mg/L, pH of 9, adsorbent dosage of 4 g/L, temperature of 25 °C, contact time of 60 min and mixture speed of 400 rpm. Furthermore, the maximum adsorption capacity was determined 80 mg/g, which was a significant value. The experimental data was analyzed using pseudo-first order, pseudo-second order and intra-particle diffusion kinetic models, which the results showed that the pseudo-second order kinetic model could better describe the kinetic behavior of the sorption process. Also, the constant rate of the pseudo-second order kinetic model was obtained in the range of 0.0218–0.0345 g/mg.min. Moreover, the adsorption equilibrium was well described using Freundlich isotherm model. Furthermore, the thermodynamic studies indicated that the sorption process of methylene blue dye using the activated carbon was spontaneous and exothermic.

Keyword: Activated carbon; lotus leaves; methylene blue dye; removal; synthetic wastewater.

1. Introduction

Environmental pollution is currently a global problem. Because of the population growth, the expansion of industry and agriculture and shortage of fresh water in the world, the need for treatment and recovery of wastewater has become critical in recent years.^{2,3} Among the various industries, the textile industry has expanded rapidly both in the world and our country, and dyeing units in the textile industry are the main environmental pollutants due to the consumption of thousands types of dye chemicals. Textile effluents usually contain a wide range of different chemical compounds. The biggest problem with these effluents is the presence of dyes and biodegradable chemicals. The most obvious characteristic of textile industry effluents is that it is colored and the two main stages of dyeing and finishing in the textile industry produce a large volume of effluent with high dye concentration.4

These dyes not only give unfavorable colors to water, but in some cases are themselves harmful compounds and

can produce other toxic products by oxidation, hydrolysis, or other chemical reactions that take place in water. Dyes are one of the most dangerous groups of chemical compounds found in industrial effluents that are of considerable importance due to the reduction of light permeability and thus disrupting the process of photosynthesis in water sources ⁵⁻⁷

These compounds also have an aesthetic negative effect on water quality for drinking and other uses⁴ and at the same time, they cause allergies, dermatitis, irritation,⁸ cancer⁹ as well as genetic mutations in humans.¹⁰ Methylene blue is the most common dye compound used for cotton, wool and silk coloring. Inhalation of this compound can cause respiratory disorders and direct exposure to it can cause permanent damage to the eyes of humans and animals, local burns, nausea and vomiting, increased sweating, mental disorders and methemoglobinemia.^{9,11,12}

Improper treatment and disposal of synthetic wastewater from the textile, dyeing, printing, and related industries has caused many environmental problems around the

world.¹³ Dye removal from wastewater is usually done by physical, physicochemical, biological or chemical methods. 14-16 The most efficient way to remove synthetic dyes from industrial effluents is the adsorption process, because the dye compounds in the effluent are easily transferred to the solid phase. 17 Besides, the adsorbent used can be regenerated and used in the adsorption process or stored after use in a dry place without direct contact with the environment. 10 Also, it has been proven that the adsorption process is a safe treatment solution due to its minimal investment cost, ease of design and operation, and insensitivity to toxic compounds. But at the same time, the use of adsorbents can be a limiting factor, because some adsorbents are expensive. To reduce the cost of preparation, the use of inexpensive materials (such as agricultural and industrial residues) for the production of activated carbon is a good option. 17,18 In addition to reducing costs, converting agricultural waste into low-cost adsorbents and solving the problem of biomass disposal has increased the value of agricultural waste even more. Carbon from agricultural wastes has advantages such as low ash content, reasonable hardness, high cross section, and a porous structure.^{4,18}

The aim of this study was to eliminate methylene blue dye from synthetic effluent using activated carbon. To this end, the impact of various parameters on the methylene blue dye removal efficiency was investigated. The structural properties of activated carbon prepared from the lotus leaves were analyzed using BET, SEM, FTIR, and EDAX analyses. Also, the kinetic, equilibrium, and thermodynamic behavior of the adsorption process were thoroughly investigated.

2. Materials and Methods

2. 1. Materials

In this study, sodium hydroxide and Hydrochloric acid (Merck, Germany) were used to adjust the pH of the solutions. Also, methylene blue dye (Merck, Germany) was used to prepare stock solutions.

2. 2. Preparation of Methylene Blue Stock Solution

To prepare the stock solution, one gram of methylene blue was dissolved in 1000 mL of water to prepare a solution of methylene blue dye at a concentration of 1000 ppm. To prepare solutions with lower concentrations, distillation of the initial stock solution was diluted twice using water.

2.3. Preparation of Activated Carbon from Lotus Leaves

To prepare activated carbon, we first collected the lotus leaves and washed it several times with water to remove the dust. After washing, the leaves are placed in an oven (dryer) at 105 °C for 2 hours to dry completely. The dried lotus leaves are placed in a furnace at 700 °C for 2 hours to produce carbon. The activated carbon is then pulverized using a grinder and granulated by sieve No. 25 (ASTM 11) and stored in plastic bottles at room temperature. They can be used as adsorbents to recover and remove methylene blue dye.

2. 4. Adsorption Tests

The methylene blue dye adsorption test was performed discontinuously in 200 mL Erlenmeyer flasks containing 100 mL of methylene blue dye solution. To adjust the initial pH of the solutions, sodium hydroxide and hydrochloric acid solutions with a concentration of 0.1 M were used. To investigate the effect of pH on the absorption of methylene blue dye, experiments were performed in the pH range of 3-11. Other conditions including initial concentration of 10 ppm, contact time of 40 min, temperature of 25 °C, adsorbent dose of 1.5 g/L and mixing speed of 400 rpm were considered constant. To mix, the sample was placed on a heater. Then the mixing temperature and speed were adjusted and the samples were mixed for a contact time of 40 min. At the end of this time, the sample was filtered using a funnel equipped with Whatman 42 filter paper, and the residual methylene blue dye in the solution was measured by a UV-vis spectrophotometer. The removal efficiency and adsorption capacity were then calculated. To evaluate the effect of other parameters such as temperature (25–50 °C), adsorbent dose (0.5–1 g/L), contact time (5–200 minutes) and dye concentration (10–100 mg/L), one of the parameters was changed and the rest of the parameters were considered constant. Also, the optimized values of the parameters in the previous step were used to investigate the effect of another parameter.

The adsorption capacity and removal efficiency of methylene blue dye were determined after determining the secondary concentration and having the primary concentration. Adsorption efficiency (R%) and adsorption capacity (q_e) of activated carbon adsorbent are obtained by the following equations:

$$R(\%) = {(C_i - C_o)/C_i} \times 100$$
 (1)

$$q_e = {\binom{C_i - C_o}{M}} \times V \tag{2}$$

2. 5. Equilibrium Behavior

The adsorption isotherm is important for describing the adsorption of molecular or ionic contaminants to the active sites of the adsorbent surface.^{20–23} In this study, three isotherm models such as Langmuir, Freundlich and Dubinin-Radishkevich models were used.

The Langmuir isotherm is based on the assumption that all adsorption sites are the same and the adsorption of contaminants on the adsorbent surface is monolayer. The linear form of the Langmuir isotherm is shown in Equation (3):²⁴

$$\frac{C_s}{q_s} = \frac{1}{q_{max}K_L} + \frac{C_s}{q_{max}} \tag{3}$$

Where, K_L is the Langmuir isotherm constant. Also, q_{max} determines the maximum adsorption capacity of the activated carbon.²³

To know the feasibility of the adsorption process, the separation parameter $R_{\rm L}$ is used, which is obtained from the following relation:

$$R_{L} = \frac{1}{1 + K_{L}C_{c}} \tag{4}$$

If the value of R_L is greater than one, equal to one, between zero and one, and less than one, it indicates that the adsorption process is unfavorable, linear, favorable, and irreversible.²³

On the other, the Langmuir constant parameter (K_L) is related to the Gibbs free energy change of the adsorption process (ΔG^o (kJ/mol)), which is determined from the following equation:

$$\Delta G^o = -RT \ln(K_L) \tag{5}$$

where R and T are the universal gas constant (8.314 J/mol K) and temperature (K), respectively.²⁵

Also, the Freundlich isotherm is an experimental model that expresses adsorption on heterogeneous surfaces. The linear form of the Freundlich isotherm is expressed as follows:^{23,24}

$$\ln q_e = \ln K_F + \left(\frac{1}{n}\right) \ln C_e \tag{6}$$

Here, K_F (mg/g (L/mg)^{1/n}) is indicator of constant relative adsorption capacity of the bond energy, and n is related to the adsorption capacity and heterogeneity of the adsorbent surface sites. A value of $\frac{1}{n}$ indicates the desirability of adsorption. Values of n > 1 indicate that the adsorption process is favorable.

Moreover, the Dubinin-Radishkevich isotherm is generally used to express the adsorption mechanism by distributing Gaussian energy on a heterogeneous surface. This isotherm is determined by Equations 7 and 8:²⁶

$$q_{s} = q_{D} \exp(-\beta_{D} \varepsilon_{D}^{2}) \tag{7}$$

$$\varepsilon_D = -RT \ln \left(1 + \frac{1}{C_i} \right) \tag{8}$$

Here, q_D is the saturation capacity of the Dubinin-Radishkevich model (mg/g), q_e is the equilibrium of the adsorbed pollutants on the adsorbent (mg/g), β_D is Dubinin-Radishkevich isotherm model constant (mol²/ KJ²), and ϵ_D is the Polanyi potential. E is the absorption energy, which is calculated as follows:

$$E = \frac{1}{\sqrt{2\beta_D}} \tag{9}$$

If E< 8 KJ/mol and 8<E<16 KJ/mol, the adsorption process is physical and chemical, respectively. Also, for E> 16 KJ/mol, the adsorption mechanism is intraparticle diffusion. 26

2. 6. Kinetics of Adsorption

Kinetic models are used to investigate the control rate of the adsorption process. To determine the adsorption kinetics of methylene blue dye using activated carbon, three models namely pseudo-first order (PFO), pseudo-second order (PSO), and intraparticle diffusion were used.

The linear and non-linear forms of the PFO kinetic model is described by Equations 10 and 11: ^{23,24, 27}

$$Ln(q_e - q_t) = Lnq_e - k_1t \tag{10}$$

$$q_t = q_s (1 - e^{-k_1 t}) \tag{11}$$

Here, q_e and q_t are the amount of adsorption capacity of adsorbed pollutants per unit weight of adsorbent at equilibrium time (mg/g), the adsorption capacity of adsorbed pollutants at time t (mg/g), respectively. Also, k_1 is the pseudo-first order kinetic rate constant (min⁻¹).^{23,24}

The linear and non-linear forms of the PSO kinetic model is also expressed as follows:²⁷

$$\frac{\mathbf{t}}{\mathbf{q}_{\mathbf{r}}} = \frac{1}{\mathbf{k}_{2}\mathbf{q}_{\mathbf{e}}^{2}} + \frac{\mathbf{t}}{\mathbf{q}_{\mathbf{e}}} \tag{12}$$

$$q_{t} = \frac{k_{2}q_{e}^{2}t}{1 + k_{2}q_{e}t} \tag{13}$$

Where, k_2 is the pseudo-second order kinetic constant (mg mol⁻¹ min⁻¹).

Another kinetic model is the intraparticle diffusion model. The adsorption process on a porous adsorbent is generally described by four steps. These steps are described as mass diffusion, film diffusion, intraparticle diffusion, and finally adsorption of contaminants on the adsorbent surface. The intraparticle diffusion model can be expressed as follows:

$$q_t = K_{id}t^{1/2} + I \tag{14}$$

Here, K_{id} (mg g^{-1} min^{-1/2}) is the intraparticle diffusion rate constant. Also, I (mg/g) is a constant, which is determined by the intercept of the plot of q_t against $t^{1/2}$.²⁸

2. 7. Adsorption Thermodynamics

Changes in the rate of adsorption with respect to temperature are explained based on thermodynamic parameters such as change in enthalpy (ΔH°), change in entropy (ΔS°) and Gibbs free energy change (ΔG°), which are obtained by using equations 15 and 16:^{29,30}

$$\Delta G^0 = -RT \ln K_c \tag{15}$$

$$\ln K_c = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \tag{16}$$

The change in Gibbs free energy in the process depends on the quantity of equilibrium constant K_c , which is expressed as follow:

$$K_{c} = \frac{C_{Ae}}{C_{e}} \tag{17}$$

In Equation (14), K_c is the equilibrium constant and C_{Ae} is the equilibrium concentration in the solid phase

(mg/L). The amount of changes in enthalpy (ΔH°) and entropy (ΔS°) are obtained by plotting In K_c versus 1/T.

3. Results and Discussion

3. 1. Determining the Properties of Activated Carbon

Various analyses including SEM, FTIR, EDAX, and BET were used to determine the physical properties of activated carbon adsorbent obtained from the lotus leaves. Figure 1 shows the SEM analysis of the activated carbon surface prepared from the lotus leaves, before and after the adsorption of methylene blue dye. Figure 1(a) shows that the activated carbon prepared from the lotus leaves before absorbing the methylene blue dye has uneven structure and a large number of adsorption channels. Then, Figure 1(b) shows the activated carbon prepared from the lotus leaves after adsorption of methylene blue dye. The adsorbent surface is uniform and the adsorption channels have disappeared.^{31,32} This uniformity and disappearance of adsorption channels in Figure 1(b) indicates the adsorption of methylene blue dye on the activated carbon adsorbent.

To evaluate the functional groups on the surface of activated carbon adsorbent, FTIR analysis was used, which

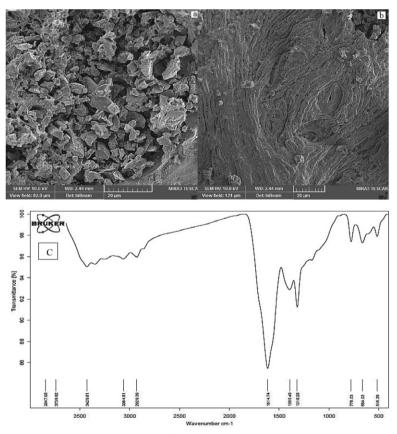
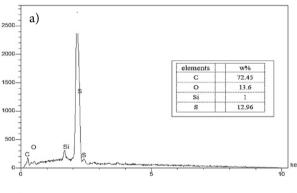


Figure 1. SEM image for activated carbon (a), activated carbon after adsorption of methylene blue dye (b), and FTIR analysis for activated carbon prepared from lotus leaves (c).

is shown in Figure 1. FTIR analysis has identified groups in different ranges. There are several peaks at 3847.08, 3739.92, 3429.81, 3064.81, 2929.39, 1614.74, 1395.49, 1318.25, 778.03, 664.03, and 516.29, which are attributed to the functional groups of O-H, O-H, O-H, C-H, C-H, C=C, C-O, C-O, C-H, O-H, and O-H, respectively.^{33–36}

Also, the EDAX analysis of activated carbon prepared from the lotus leaves before and after the methylene blue dye adsorption process is shown in Figure 2. According to Figure 3(b), before the adsorption process, activated carbon contains elements such as carbon (72.45%), oxygen (13.6%), silicon (1%) and sulfur (12.96%). After the methylene blue dye adsorption process, the amount of these elements changed, which includes carbon (60.62%), oxygen (32.61%), silicon (0.5%), and sulfur (6.27%). Changes in the amounts of activated carbon constituents before and after the methylene blue dye adsorption process can be due to the adsorption of the dye by activated carbon.³⁷



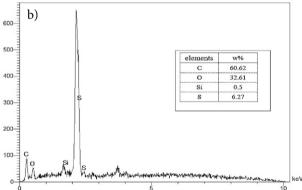


Figure 2. EDAX analysis (a) Activated carbon produced from lotus leaves before the adsorption process and (b) Activated carbon after the sorption of methylene blue dye

Properties such as specific surface area, average pore volume, and pore diameter are determined using BET analysis and the results are presented in Table 1. According to the results, the specific surface area of activated carbon, the average pore volume and the pore diameter obtained from BET analysis were determined 64.415 g/m², 0.056948 g/cm³ and 35.3633 °A, respectively. These values indicate that the activated carbon prepared from the lotus leaves

Table 1. Surface properties of activated carbon prepared from the lotus leaves using BET analysis.

Properties	Values
Analyzed activated carbon mass	0.5588 g
Specific surface area	64.4152 g/m ²
Average pore volume	0.056948 g/cm ³
Average pore diameter	35.3633 °A

has a good specific surface area and pore volume. Also, the average pore diameter indicates that the activated carbon has a mesoporous structure, because the pore diameter is in the range of 20 to 500 °A.

3. 2. The Effect of Different Parameters on the Adsorption Process

3. 2. 1. pH Effect

Solution pH is one of the most important and effective parameters in controlling the adsorption process. Also, it gives the valuable information regarding the mechanism of adsorption. The effect of pH on the adsorption efficiency of methylene blue dye by using activated carbon prepared from the lotus leaves is shown in Figure 3. The results show that by increasing the initial pH, the methylene blue dye adsorption efficiency is increased and the maximum yield is obtained approximately at the initial pH of 9. This result can be described according to the cationic properties of methylene blue dye. At low initial pHs (pH < 5), the adsorption efficiency of methylene blue dye using a prepared adsorbent is low, indicating that acidic pHs are not suitable for adsorption of methylene blue dye. This is because at acidic pHs the adsorbent surface is positively charged and, as a result, the methylene blue cationic dye is repelled by the positively charged adsorbent surface. Also, by increasing the initial pH, the percentage of methylene blue dye adsorption using the adsorbent increases, because by in-

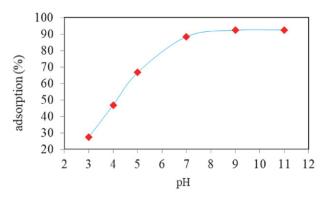


Figure 3. Effect of pH on methylene blue dye removal efficiency (adsorbent dose of 1.5 g/L, contact time of 40 min, initial dye concentration of 10 ppm, temperature of 25 °C and mixing speed of 400 rpm).

creasing pH, negative charges on the adsorbent surface increases and an attractive force is created between the adsorbent surface and the cationic dye.³⁸ Therefore, the optimal pH for the sorption of methylene blue dye from aqueous solution using activated carbon was obtained as 9.

3. 2. 2. Effect of Temperature and Contact Time

The effect of different contact times (5-200 min) at 25, 35, 45 and 55 °C on the removal efficiency of methylene blue dye by activated carbon is shown in Figure 4. The results show that during the initial contact time (5 min), the adsorption of methylene blue dye was high at 25 °C, which is equal to 43.63%. By increasing the temperature up to 55 °C, the removal efficiency decreases and reaches 34.64%. Thus, by increasing the temperature, the adsorption efficiency decreased, which indicates that the adsorption process is exothermic. The decrease in removal efficiency with increasing temperature is due to the weakening of the adsorption forces between the active sites of the activated carbon adsorbent and the methylene blue dye. In this case, methylene blue dye is released in the solution phase. Thus, the removal efficiency decreases. However, by increasing the contact time, the removal efficiency increased and reached equilibrium after 60 min reaction time. Methylene blue dye adsorption efficiency remained uniform after 60 min. Because in this case, the adsorption sites on the adsorbent surface are saturated and it is observed that the removal efficiency has not changed much. Therefore, the maximum methylene blue dye removal efficiency was obtained at a contact time of 60 min and a temperature of 25 °C. Under these conditions, the adsorption efficiency of methylene blue dye was 93.67%.

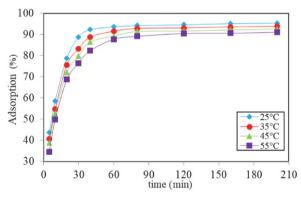


Figure 4. Effect of temperature and contact time on the removal efficiency of methylene blue dye by activated carbon (conditions: pH of 9, adsorbent dose of 1.5 g/L, initial dye concentration of 10 ppm, and mixing speed of 400 rpm).

3. 2. 3. Effect of Initial Concentration of Methylene Blue Dye

The effect of methylene blue dye concentration on removal efficiency and adsorption capacity at constant pH

of 9, adsorbent dose 1.5 g/L, contact time of 60 min, temperature 25 °C, and mixing speed 400 rpm are shown in Figure 5. The effect of methylene blue dye concentration in the range of 10–100 ppm has been selected.

As shown in the figure, by increasing the concentration from 10 to 100 ppm, the removal efficiency decreases. To check the initial concentration parameter, the amount of concentrations is different and the amount of absorbent dose is constant. In this case, by increasing dye concentration, the amount of methylene blue dye in the aqueous solution increases relative to the adsorbent dose and there are fewer adsorption sites for methylene blue dyes to be placed on the adsorbent surface, and as a result, the removal efficiency is decreased.

On the other hand, in Figure 5, by increasing the concentration from 10 to 100 ppm, the adsorption capacity is increasing. As the concentration of methylene blue dye in aqueous solution increases, the desired amount of contaminant increases. As a result, the contact of methylene blue dyes increases, which causes the methylene blue dye to be adsorbed more on the activated carbon sites, thus increasing the adsorption capacity.

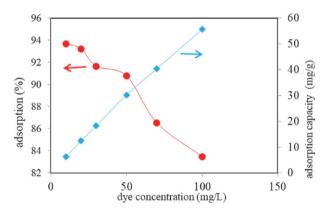


Figure 5. Effect of initial methylene blue dye concentration on removal efficiency and adsorption capacity of methylene blue dye (pH equal to 9, adsorbent dose 1.5 g/L, contact time 60 min, temperature 25 °C and mixing speed 400 rpm).

3. 2. 4. Effect of Activated Carbon Adsorbent Dose

The values of adsorption capacity and methylene blue dye removal efficiency at different doses of activated carbon are shown in Figure 6. By increasing the dose of activated carbon adsorbent from 0.5 to 10 g/L, the removal efficiency has increased from 82.84% to 98.032%, while adsorption capacity $(q_{\rm e})$ presents an inverse trend. Increasing the removal efficiency is due to the increase in surface area and the increase in adsorption sites available for methylene blue dye.

The decrease of adsorption capacity (q_e) from 16.568 to 0.98032 mg/g is observed with increasing the adsorbent dose from 0.5 to 10 g/L, which is due to the competition

between contaminants and adsorbents.³⁹ By increasing the adsorbent dose, the adsorbent surface becomes saturated and reduces the adsorption capacity (q_e).

When the dose of activated carbon adsorbent from the lotus leaves was 4 g/L, the removal efficiency and adsorption capacity (q_e) were 97.59% and 2.439 mg/g, respectively. At adsorbent dose of above 4 g/L, there was no significant increase in methylene blue removal efficiency and the diagram is almost constant and the adsorption capacity (q_e) is also reduced. Therefore, according to the adsorption capacity (q_e) and removal efficiency, the adsorbent dose of 4 g/L was determined as the optimal value.

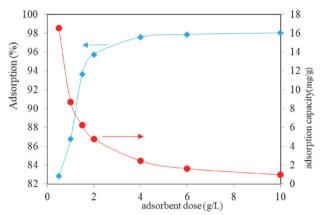


Figure 6. Effect of activated carbon adsorbent dose on removal efficiency and adsorption capacity of methylene blue dye (pH equal to 9, initial concentration 10 ppm, contact time 60 min, temperature 25 °C and mixing speed 400 rpm).

3. 3. Equilibrium Study of Adsorption Process

Three isotherm models such as Langmuir, Freundlich, and Dubinin Radushkevitch (D-R) were used to remove methylene blue dye using the activated carbon adsorbent prepared from lotus leaves. Isotherm models were investigated at different concentrations (10–100 ppm) of methylene blue, and other conditions were kept constant, including pH of 9, contact time of 60 min, temperature of 25 °C, adsorbent dose of 1.5 g/L, and mixing speed of 400 rpm.

The Langmuir, Freundlich, and Dubinin-Radushkevitch (D-R) isotherm models are plotted in Figure 7, and their constant values are given in Table 2. According to the Langmuir isotherm model, the R_L value was in the range of 0.729-0.44, which indicates that the adsorption process of methylene blue dye with activated carbon adsorbent is favorable. Also, the maximum adsorption capacity of the activated carbon was obtained 80 mg/g. In addition, according to the values of the coefficient of determination obtained for all three models, the Freundlich isotherm model could better describe the equilibrium behavior of the methylene blue dye adsorption process than other isotherm models. Also, the value of parameter n using the Freundlich isotherm was equal to 1.514, which indicates that the adsorption process is favorable because its value is greater than one. Moreover, the value of parameter K_f was determined 9.55 mg/g(L/mg)^{1/n}. Furthermore, according to the amount of energy E obtained using the D-R isotherm model (1.207 KJ/mol), the adsorption mechanism of methylene blue dye with the adsorbent is physical. Be-

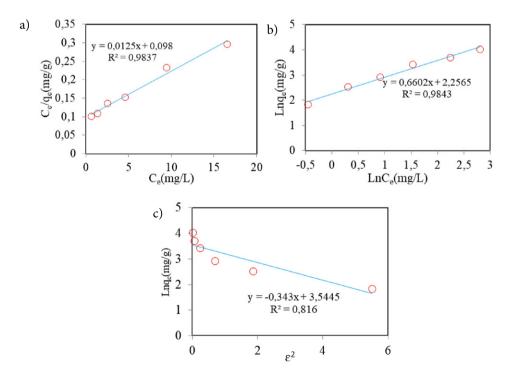


Figure 7. Langmuir (a), Freundlich (b) and D-R (c) isotherms for the uptake of methylene blue dye using the activated carbon

Table 2. Values and constants of adsorption isotherms.

Isothermal models	Quantities	Methyl violet dye
	q _{max} (mg/g)	80
	$K_L (L/mg)$	0.127
Langmuir	ΔG° (kJ/mol)	-5.112
C	\mathbb{R}^2	0.9837
	R_{L}	0.729 - 0.44
	n	1.514
Freundlich	$K_f (mg/g(L/mg)^{1/n})$	9.5496
	\mathbb{R}^2	0.9843
	E (KJ/mol)	1.207
Dubinin Radushkevitch	$q_D (mg/g)$	34.622
(D-R)	$B \times 10^{-6} (\text{mol}^2/\text{J}^2)$	0.343
	\mathbb{R}^2	0.816

sides, the maximum adsorption capacity using the D-R isotherm was obtained 34.62 mg/g. 40,41 In addition, the Gibbs free energy (ΔG°) using the Langmuir model was determined –5.112 KJ/mol, which indicates the spontaneity degree of the sorption process. Also, negative value of ΔG° shows a favorable sorption process. 25

The maximum sorption capacity obtained in this research for the sorption of methylene blue was compared to previous studies and the results are presented in Table 3. According to this table, the maximum sorption capacity of the activated carbon used in this study was

Table 3. Comparing the maximum sorption capacity of different adsorbents in the removal of methylene blue from aqueous media

Adsorbent	Maximum sorption capacity (mg/g)	Ref.
Palm tree sawdust	54	4
Sour lemon sawdust	52.4	4
Eucalyptus sawdust	53.5	4
Kaolin/CuFe ₂ O ₄ nanocomposite	120.48	17
activated carbon prepared by Ficus caricabast	47.62	42
magnetic cellulose/graphene oxide composite	70.03	43
Activated carbon	1.23	44
Activated carbon prepared by lotus leaves	80	Present study

obtained 80 mg/g, which was comparable with other adsorbents in removing methylene blue from aqueous media

3. 4. Kinetic Study of Adsorption

Figure 8 illustrates pseudo-first order, pseudo-second order, and intraparticle diffusion kinetic models. The graphs drawn include the linear equation and the coefficient of determination (\mathbb{R}^2). The amounts of models were calculated from the obtained linear equations and the re-

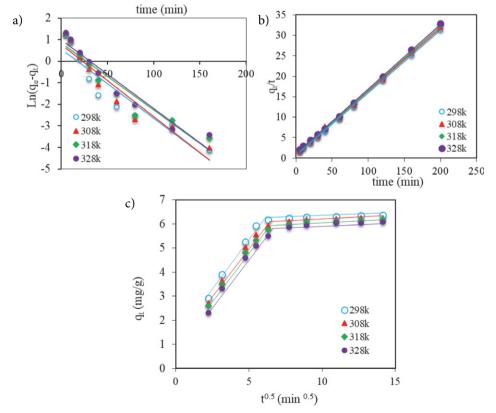


Figure 8. The linear forms of PFO (a), PSO (b) and intraparticle diffusion (c) kinetic models at different temperatures and times.

sults are reported in Table 4. The constant rate of pseudo-first order kinetics (k_1) , the constant rate of pseudo-second order kinetics (k_2) , the constant rate of intraparticle diffusion kinetics (K_{dif}) , and the equilibrium adsorption capacity $(q_{e.theoretical})$ were calculated for all temperatures. ^{45, 46}

The calculated adsorption capacity values ($q_{e.theoretical}$) using the pseudo-first order kinetic model are very different from the laboratory adsorption capacity values ($q_{e.exp}$). Whereas, the calculated adsorption capacity values ($q_{e.exp}$) are very close to the laboratory adsorption capacity values ($q_{e.exp}$) of the pseudo-second order kinetic model. In addition, R^2 values of the pseudo-first order kinetic models and intraparticle diffusion are lower than the pseudo-second order kinetic model. Also, the constant rate of pseudo-first order kinetics (k_1) at all temperatures are less than the constant rate of pseudo-first order kinetics (k_2). Moreover, a comparison between the PFO and PSO kinetic models and the experimental data

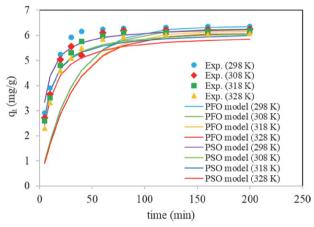


Figure 9. Fitting non-linear forms of kinetic models to experimental data

is shown in Figure 9. As shown, the PSO kinetic model is well fitted with the experimental data compared to the PFO model. Therefore, it can be concluded that the pseudo-second order kinetic model is more suitable for the mechanism of adsorption of methylene blue dye with activated carbon adsorbent prepared from lotus leaves. 47 Besides, the intraparticle diffusion kinetic model describes that the sorption process of methylene blue is nonlinear and shows that more than one mechanism contributes to the dye sorption on the surface of activated carbon. The initial linear part of the figure has a higher slope and is attributed to the film diffusion in which methylene blue dye is transported to the adsorbent surface. This step is performed at a high rate. The second linear part has a lower slope, which demonstrates dye diffusion into the activated carbon.⁴⁸

3. 5. Study of Thermodynamics of Adsorption Process

Table 5 lists the values of ΔG° , ΔH° and ΔS° at different temperatures. Figure 9 also shows LnK_D versus 1/T for the sorption of methylene blue dye using activated carbon at different temperatures.

 ΔG° value at 25 °C was –5.673 KJ/mol, and enthalpy change in the range of 25–55 °C was –19.671 KJ/mol, which indicates that the methylene blue dye removal process was spontaneous and exothermic. Also, the ΔG° value using the thermodynamic study was comparable to the value obtained by the Langmuir model (–5.112 KJ/mol). Moreover, the value of ΔS° in the temperature range of 25–55 °C was equal to –47.207 KJ/mol, which shows the irregularity and randomness of the methylene blue dye adsorption process and shows the physical nature of the methylene blue dye removal process with activated carbon adsorbent.

1.5196

1.2754

kinetic models	Parameter	Temperature (55 °C)	Temperature (45 °C)	Temperature (35 °C)	Temperature (25 °C)
	\mathbb{R}^2	0.9348	0.9116	0.9129	0.8784
pseudo-first order	$k_1 \text{ (min}^{-1})$	0.0319	0.0311	0.0334	0.0322
	$q_{e.theoretical} (mg/g)$	2.6564	2.3094	2.1593	1.7550
	$q_{e.exp}$ (mg/g)	6.078	6.178	6.256	6.364
	\mathbb{R}^2	0.9995	0.9996	0.9992	0.9995
pseudo-second order	k ₂ (g/mg.min)	0.0218	0.0254	0.0242	0.0345
	q _{e.theoretical} (mg/g)	6.3451	6.4061	6.4977	6.5402
	$q_{e.exp.}$ (mg/g)	6.078	6.178	6.256	6.364
	\mathbb{R}^2	0.8863	0.8366	0.8514	0.9776
intraparticle diffusion	$K_{id,1}$ (mg/gmin ^{1/2})	0.0328	0.0263	0.0213	0.0184
	I_1	5.6348	5.8178	5.9667	6.1099
	\mathbb{R}^2	0.9712	0.977	0.8596	0.9672
	$K_{id,2}$ (mg/gmin ^{1/2})	0.7823	0.7844	0.6711	0.8195

Table 4. Values of kinetic models at different temperatures and times.

 I_2

0.7711

0.9976

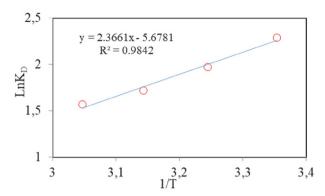


Figure 10. $\rm LnK_D$ versus 1/T diagram for the sorption of methylene blue dye with activated carbon at different temperatures

Table 5. Values of thermodynamic parameters of methylene blue dye adsorption by activated carbon at different temperatures.

Temperature	K _D	ΔG° (KJ/moL)	ΔH° (KJ/moL)	ΔS° (KJ/moL)
25 °C	9.864	-5.673		
35 °C	7.194	-5.055	10.651	45.005
45 °C	5.575	-4.545	-19.671	-47.207
55 °C	4.802	-4.28		

4. Conclusion

In this study, the adsorption process of methylene blue dye using activated carbon prepared from the lotus leaves was performed discontinuously. To prepare activated carbon adsorbent, lotus leaves were used and SEM, FTIR, EDAX, and BET analyses were done before and after removal of methylene blue dye with activated carbon adsorbent. BET analysis showed that the specific surface area of activated carbon adsorbent was high. The adsorption results showed that the highest adsorption efficiency was obtained at pH 9, 10 ppm dye concentration, 60 min, and 25 °C, in which the adsorption efficiency was 97.59%. Among the pseudo-first order, pseudo-second order, and intraparticle diffusion models, the pseudo-second order kinetic model better described the mechanism of the adsorption process. Also, three isotherm models including Langmuir, Freundlich, and Dubinin Radushkevitch (D-R) isotherms were investigated. Among these models, the Freundlich isotherm with a higher R² value was able to better express the equilibrium behavior of the adsorption process. Moreover, the highest adsorption capacity of methylene blue dye was obtained 80 mg/g. Furthermore, the thermodynamic study showed that the adsorption process of methylene blue dye by activated carbon is exothermic and spontaneous.

Conflict of Interests Statement

The authors declare that there is no conflict of interests.

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Povzetek

Preučili smo odstranjevanje barvila metilensko modro iz vodnih raztopin z uporabo aktivnega oglja pripravljenega iz lotusovih listov. Eksperimenti so bili izvedeni šaržno. Površinske lastnosti aktivnega oglja smo analizirali s pomočjo SEM, FTIR, EDAX in BET. Maksimalno adsorpcijsko učinkovitost 97.59 % smo dosegli pri koncentraciji barvila 10 mg/L, pH vrednosti 9, koncentraciji adsorbenta 4 g/L, temperaturi 25 °C, kontaktnem času 60 min in mešanju pri 400 rpm. Maksimalna adsorpcijska kapaciteta je znašala 80 mg/g. Eksperimentalne podatke smo analizirali s kinetičnimi modeli psevdo-prvega in psevdo-drugega reda ter modelom znotraj delčne difuzije. Rezultati so pokazali najboljše ujemanje s kinetičnim modelom psevdo-drugega reda s kinetično konstanto v območju 0.0218–0.0345 g/mg.min. Ravnotežje smo dobro opisali z Freundlichovo adsorpcijsko izotermo. Proces adsorpcije barvila metilensko modro na aktivno oglje je spontan in eksotermni proces.



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