



Eco-Friendly Activated Carbon Synthesized from Date Pits and Application in Water Treatment to Remove Organic Dyes



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Received: 07-15-2025

Revised: 09-26-2025

Accepted: 11-04-2025

Citation: M. F. Abdulrahman, I. A. Mawlood, N. N. Hilal, W. M. Saod, and M. I. AlBiajawi, "Eco-friendly activated carbon synthesized from date pits and application in water treatment to remove organic dyes," *Int. J. Environ. Impacts.*, vol. 9, no. 1, pp. 74–84, 2026. <https://doi.org/10.56578/ije090107>.



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Abstract: Chemical dyes are routinely discharged into ecosystems via textile industry effluents and landfill leachates. Adsorption using engineered adsorbents presents a viable strategy for pollutant removal in water treatment. Activated carbon (AC) and carbon nanoparticles are composite materials that integrate nanomaterials, rendering them less susceptible to these processes. This study involved preparing and characterizing AC using UV-Vis, fourier-transform infrared (FTIR), X-ray diffraction (XRD), and scanning electron microscopy (SEM) techniques. We subsequently assessed its capacity to remove methylene blue (MB) under varying conditions of pH, initial dye concentration, adsorbent dosage, and contact time. The dye is often utilized in the textile and chemical industries. The adsorbent achieved a removal efficacy of 99.9% under optimal conditions: a temperature of 25 °C, a pH range of 7–9, and a contact time of 60–120 minutes. The removal process was characterized by pseudo-second-order kinetics and the Freundlich isotherm model. The results indicated that the adsorbent's surface was heterogeneous, consisting of many layers. The calculated thermodynamic parameters were $\Delta G^\circ = -4.24 \text{ kJ/mol}$, $\Delta H^\circ = -0.0975 \text{ kJ/mol}$, and $\Delta S^\circ = -0.3125 \text{ kJ/kg/K}$.

Keywords: Activated carbon; Date pits; Economic; Removal of organic dyes

1 Introduction

Rapid industrial expansion has exacerbated environmental pollution, presenting a major global challenge [1–3]. The disposal of waste materials by dyeing industries into water bodies causes pollution of drinking and agricultural waters. Given that dyes are often toxic, mutagenic, and carcinogenic, treating dye-contaminated wastewater is a critical environmental challenge [4–6]. Color pollutants are difficult to remove due to their high solubility in water [7]. Various conventional methods, such as adsorption, coagulation, membrane filtration, and oxidation, have been evaluated [8]. Among these, adsorption is preferable due to its low cost, and it is more effective for low concentrations of contaminants [7]. Activated carbon (AC) is a well-known adsorbent and is used for dye removal in water bodies [9]. AC treatment has proven effective for wastewater remediation. This effectiveness stems from its porous structure and large surface area, which make AC one of the most widely used adsorbents [10]. Because of its porous structure and large surface area, AC is one of the most widely used adsorbents for removing a variety of pollutants from coupling water [11]. Commercially available AC is derived from coconut shells, wood, and coal. However, its high cost has still created interest in producing low-cost coconut shells. Consequently, research has shifted toward low-cost alternative adsorbents for methylene blue (MB) removal. Agricultural waste products like coir, palm nut shells, maize, wheat, peas, lentils, and so on are available as both low-cost adsorbents and easily available raw materials for preparing novel adsorbents [12, 13]. There is increasing interest in developing low-cost adsorbents from agricultural waste products such as palm and rice husks, sawdust, coir, bamboo, jute, etc. The production of AC from agricultural waste

is considered cost-effective because it is an unavoidable byproduct of agricultural processing and is widely available in developing countries [14].

Although many low-cost biomass wastes are available for AC production, their utilization remains limited. Recently, many abundant, renewable, and low-cost materials, such as animal bones, plant biomass, etc., with high carbon content, have been used for AC production [15]. Date palm tree (*Phoenix dactylifera L.*) cultivation has gained significance due to its high adaptability to arid regions and good economic returns. Date pits, an environmental residue with high carbon content, have been investigated both environmentally and economically [16]. Physicochemical and chemical activation methods were used [17].

Development methods such as temperature, time, and chemical agents were optimized. Mesoporous activated carbon (MAC) has good hydrophilicity, low density, and excellent dye removal [18]. Mesoporous activated carbon derived from date pits (DPAC) exhibits high surface area and structural integrity. The surface modification of DPAC changes its physical and chemical properties. In this study, we aimed to produce AC from date pits to absorb cationic dye (MB) from water-based solutions. The effects of time, pH, AC dosage, and initial dye concentration were investigated in batch tests. Thermodynamics, kinetics, and isotherms were carefully examined for AC extracted from date pits. To evaluate the practicality and efficacy of the adsorption process, various thermodynamic parameters, including ΔG° , ΔH° , and ΔS° , were computed at different temperatures.

2 Materials and Methods

2.1 Materials

Materials used in this study include date pits, zinc chloride, MB, hydrochloric acid, and distilled water. Samples of date pits were collected from the local area. All other compounds were analytical reagents (AR) grade and used unpurified.

2.2 Collection and Preparation of Date Pits

The date pits utilized as raw material in this investigation were obtained from a molasses factory in Hit City, Anbar Governorate, Iraq. These date pits were collected, washed thoroughly with water to remove any adhering dirt, and dried at a temperature not exceeding 60 °C before carbonization. After drying, the Date pits were crushed using a laboratory ball mill and then sieved to obtain particles in the 40–60 mesh size range.

2.3 Activated Carbon (AC) Preparation Process

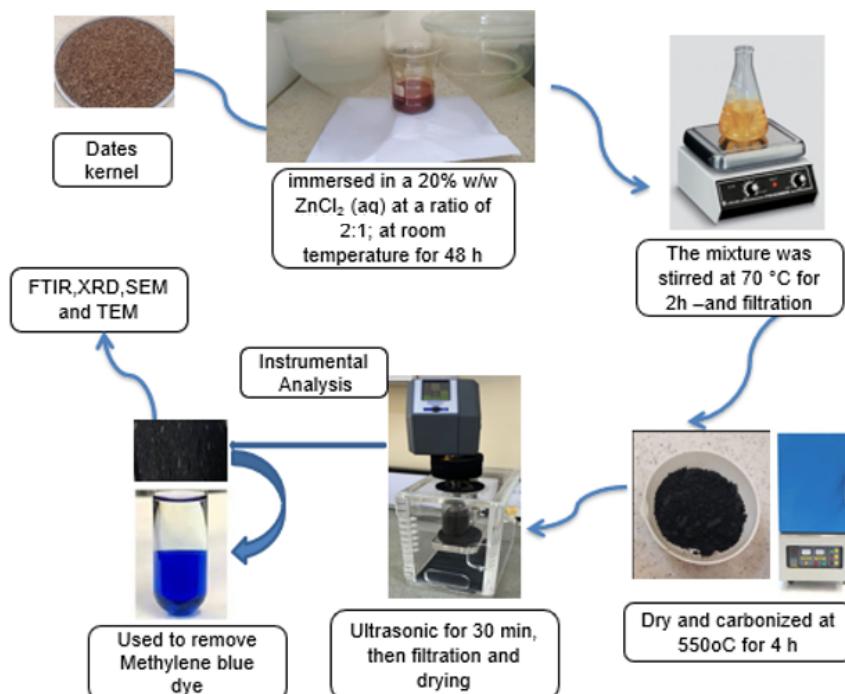


Figure 1. The process used to produce the date pits activated carbon (DPAC)

AC is mainly derived from Date pits with this technique. The biomass date pits were immersed in a 20% w/w $ZnCl_2$ solution prepared in a 2:1 ratio to produce AC. The mixture was agitated for 2 hours at 70 °C, then allowed

to stand at room temperature for a further 48 hours. After filtering, the mixture underwent carbonization in a furnace maintained at 400–500 degrees Celsius for a duration of 2 hours, followed by cooling to ambient temperature. Subsequent to the treatment of the carbonized material with 0.1 N hydrochloric acid, it was filtered and thoroughly rinsed several times with deionized water to eliminate any residual impurities. This procedure guaranteed the purity of the end product, AC. The AC was dried overnight at 105 °C, thereafter crushed, and sieved through a mesh with a size of 16 °C to 20 °C [19]. Figure 1 shows the primary method used to produce the AC from the dates.

2.4 Characterization of Adsorbent

The analysis of the characteristics and quality of the prepared adsorbents, in terms of surface morphology, structure, and chemical composition, was carried out prior to application using several characterization techniques. Field emission scanning electron microscopy (FESEM) revealed the surface morphology of the precursors. To further explore the chemical functionality, the chemical compositions of the adsorbents were investigated utilizing Fourier-transform infrared (FTIR) spectroscopy Bruker Germany in the range of 4000–400 cm⁻¹. The crystalline phase and structure of the AC produced was characterized by X-ray diffraction (XRD) (Siemens Model No S2 P-660 D 5000) system using CuK α radiation ($\lambda = 1.54 \text{ \AA}$), Differential (FESEM) thermal analysis Mettler-Toledo instrument (USA) and transmission electron microscopy (TEM) [20–22].

2.5 Adsorption Experiments

In 50 mL tubes, a 10 mL aqueous solution with varying MB concentrations (0.5–15 mg/L) was prepared. The adsorbent was employed under varying DPAC conditions (mass range: 10–60 mg), pH (4–9), and contact duration (15–180 min) to determine the optimal adsorption conditions. Subsequent to adsorption, the solid-liquid mixtures were subjected to centrifugation at 5,000 rpm (about 2,800 $\times g$) for 10 minutes using a [FC5515] centrifuge. The supernatant was then decanted and meticulously filtered. The concentrations of metal ions in the filtrate were quantified using UV-Vis spectroscopy (UV-Cary 60, Agilent), with appropriate instrument parameters (wavelengths: Ni 664.0 nm). Calibration standards (0.01–1 mg/L) were established using validated reference materials, with quality control samples evaluated every 10 samples to ensure measurement accuracy ($R^2 > 0.999$ for calibration curves).

The measured concentrations were used to determine the adsorption capacity, q_e (Eq. (1)), and the removal efficiency, %R (Eq. (2)).

$$q_e = \frac{V}{(C_0 - C_e)} \quad (1)$$

$$\%R = 100 \times \frac{(C_0 - C_e)}{C_0} \quad (2)$$

C_0 shows the starting concentration of MB, and the ending concentration, or equilibrium, is shown by C_e (mg/L), where m is the adsorbent's mass in grams, and V is the solution's volume in liters. The Langmuir and Freundlich sorption isotherms were calculated by batch tests with adsorbent concentrations ranging from 0.5 to 15 mg/L, dye concentrations of 10 mg/mL, and a volume of 10 mL. For the isotherm equations, Eqs. (3) and (4) represent the linear form of Langmuir and Freundlich respectively.

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

$$\log q_e = \log K_f + \left(\frac{1}{n} \right) \log C_e \quad (4)$$

K_L and q_m are the Langmuir constants, K_f is the Freundlich constant, and $1/n$ is a dimensionless Freundlich model function [22, 23].

2.6 The First and Second Pseudo-Order Models

A linear variation of the Lagergren equation, the pseudo-first-order kinetic model, is provided by:

$$q_t = q_e (1 - e^{-k_1 t}) \quad (5)$$

or in the linear form can be expressed as follows:

$$\ln (q_e - q_t) = \ln (q_e) - k_1 t \quad (6)$$

The pseudo-first-order kinetic model describes adsorption based on the linearity of the plot of $\ln(q_e - q_t)$ versus time t , where q_e and q_t represent the adsorbed dye amounts at equilibrium and time t , respectively, and k_1 (1/min) is the rate constant. A straight-line fit with a slope of (-1) confirms the applicability of this model.

The following expression represents the pseudo-second-order kinetic model:

$$q_t = q_e^2 k_1 t + 1 \quad (7)$$

The equation can be linearized as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (8)$$

The pseudo-second-order adsorption kinetics is defined by the rate constant k_2 , with a linear plot of t/q_t against t validating the model's applicability.

The intraparticle diffusion model delineates a multi-stage adsorption process, comprising 1. initial solute transport from the particle surface to internal destinations, followed by 2. diffusion through the particle internal layers.

$$q_t = k_{id} t^{1/2} + C \quad (9)$$

where, C is a constant that indicates the thickness of the interior layer and k_{id} is the intraparticle diffusion rate constant ($\text{mg/g}\cdot\text{min}^{1/2}$), the higher the influence of the surface diffusion resistance.

2.7 Thermodynamics Study

Temperatures of 298, 303, 313, and 323 K were used to study the thermodynamics of the adsorption process. Using Eq. (10), the adsorption potential ΔF was determined.

$$\Delta F = -RT \ln K \quad (10)$$

T stands for the absolute temperature in Kelvin, and R represents the gas constant in joules per mole. Thermodynamic parameters ΔH° , ΔG° , and ΔS° were determined using the Lacey Eq. (11):

$$\ln K = \frac{\Delta H^\circ}{RT} - \frac{\Delta G^\circ}{R} \quad (11)$$

3 Results and Discussion

3.1 Physicochemical Properties of Activated Carbon (AC)

AC was produced from date pits through a chemical activation process by using zinc chloride. The produced AC were characterized and evaluated as adsorbents for MB dye removal from aqueous solutions. The yield, surface area, porosity, and the chemical groups of the produced AC at optimal conditions were studied. DPAC was produced by carbonization at 550 °C. The analysis of the characteristics and quality of the prepared adsorbents in terms of surface morphology, structure, and chemical composition was carried out before application via several characterization techniques.

The FTIR of the synthesized AC in the 600–4000 cm^{-1} region is shown in Figure 2. The absorbance bands exhibit many peaks at different wavenumbers, corresponding to distinct functional groups. At around 3070 cm^{-1} , a weak band is attributed to aromatic compounds (=C–H).

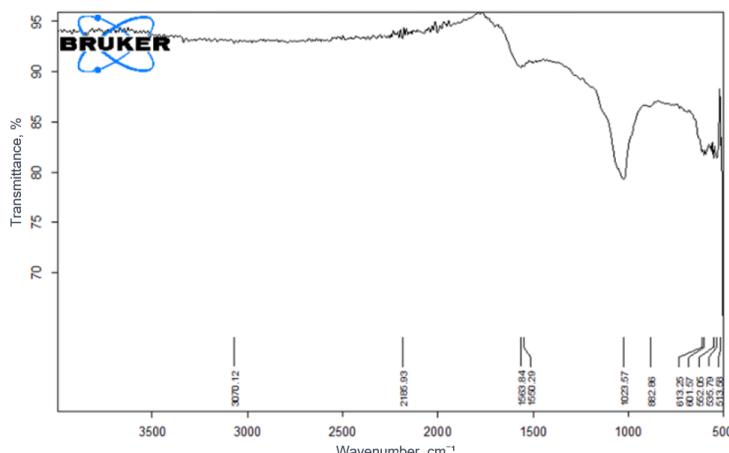


Figure 2. The Fourier-transform infrared (FTIR) spectrum of the synthesized date pits activated carbon (DPAC)

Additionally, the C=N and C=C stretching can be attributed to the vibrational bands at 1564 and 1550 cm^{-1} , respectively. The stretching vibration of the atomic groups C—O—C was typically attributed to the peak measured at 1023 cm^{-1} . Alkyl C—H bond bending vibrations can be seen across the fingerprint region, for instance, at 882 cm^{-1} [24]. These findings suggest that there are many functional groups on the surface of the synthesized AC.

The surface morphology of precursors was inspected using scanning electron microscopy (SEM) and TEM.

SEM enables the visualization of the surface topography of a sample. By bombarding the sample with a focused electron beam, electrons emitted from the sample surface can be detected to generate an image that reveals surface morphology. Flexible sheet-like structures of the samples confirmed the uniform dispersion of AC on the surface of the matrix carbon (Figure 3).

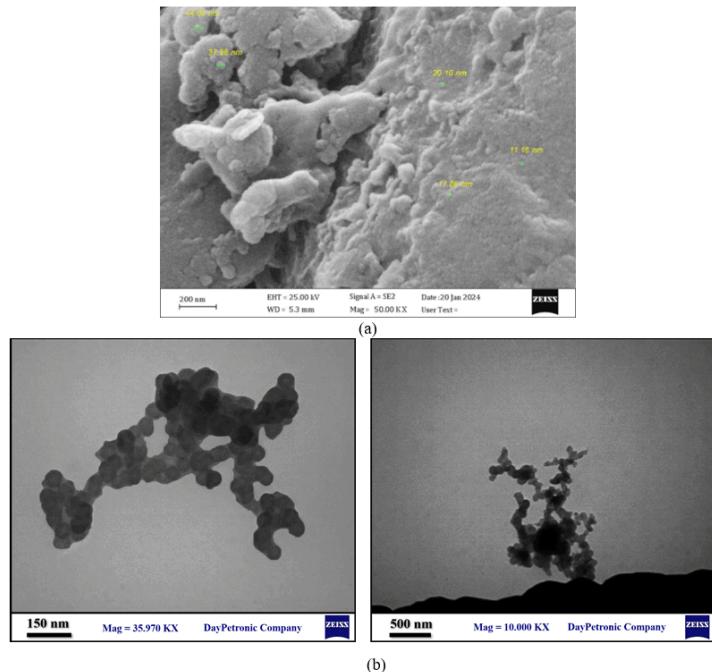


Figure 3. Images of date pits activated carbon (DPAC): (a) scanning electron microscopy (SEM); (b) transmission electron microscopy (TEM)

XRD is a technique that involves the interaction of X-rays with a crystalline solid and is usually used to determine the crystal structure. The XRD pattern obtained (Figure 4) provides a fingerprint for identifying the crystal phase. Significant peaks at $2\theta \approx 15.3^\circ$, 28.7° , and 43.1° indicate a particular crystal lattice configuration. Low-intensity peaks at $2\theta > 60^\circ$ indicate the presence of small secondary phases or lattice imperfections. AC has a nanocrystalline architecture with low amorphousness [25, 26].

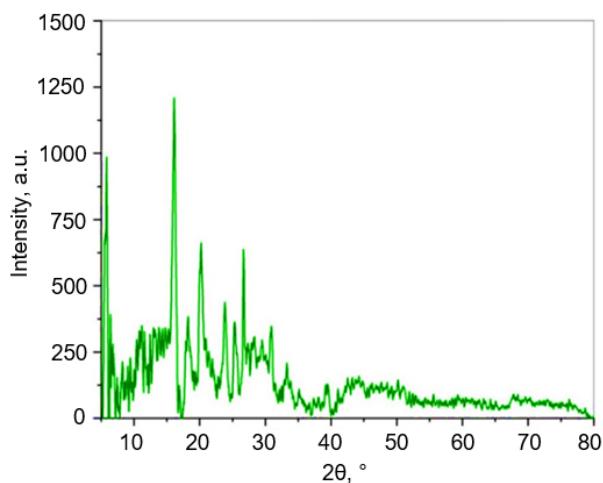


Figure 4. The X-ray diffraction (XRD) pattern obtained for date pits activated carbon (DPAC)

3.2 Adsorption Study

The pH of the solution shown affected the adsorption effectiveness of all sorbents (Figure 5). The removal of MB was effective across a wide pH range because the dye is positively charged and the sorbent's charge changes with pH. Under reduced pH (acidic conditions), the protonation of functional groups could reduce their magnetic attraction, whereas elevated pH (alkaline conditions) promotes deprotonation, hence enhancing the affinity between dye and sorbent through forces [27]. DPAC demonstrates this trend by maintaining high efficiency across a range of pH values, owing to its strong structure and oxygen-rich surface. These results support the findings. These results align with prior findings linking stable adsorption across pH ranges to sorbents possessing diverse active sites [28].

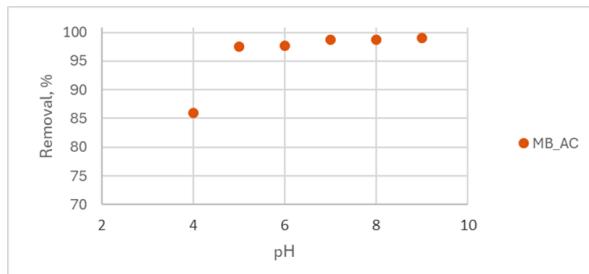


Figure 5. The impact of solution pH on date pits activated carbon (DPAC) to remove methylene blue (MB)

The influence of adsorbent dosage on the removal effectiveness of MB was evaluated utilizing DPAC within a range of 0.01–0.06 g (Figure 6). A nearly linear rise in MB adsorption was noted with increasing AC dosage, with optimal removal ($\geq 95\%$) at 0.06 g. This tendency corresponds with fundamental adsorption principles: increased doses yield a larger surface area and additional active sites for dye adsorption [29]. The observed linearity indicates unsaturated adsorption capability at lower doses, aligning with physisorption-dominated processes [30].

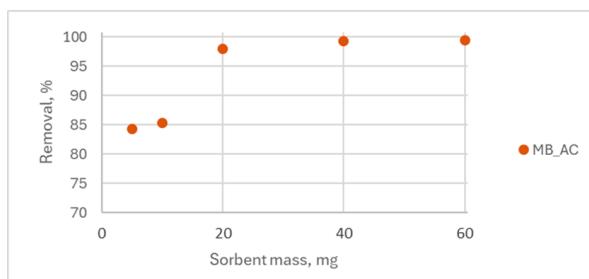


Figure 6. Effect of date pits activated carbon (DPAC) mass on the removal of methylene blue (MB)

The saturation point at 0.06 g signifies the total occupation of accessible binding sites for the specified dye concentration (5 mg/L). Furthermore, exceeding this dosage would yield negligible efficiency improvements due to site saturation or particle aggregation, which diminishes the effective surface area [31].

In the concentration range examined, DPAC removed at least 90% of MB dye, and across all concentrations, the material typically achieved $\sim 100\%$ removal (Figure 7). For every concentration that was tested, the computed adsorption masses (q_e) are shown in Table 1 shows the calculated adsorption masses (q_e), which show both the time it takes for the adsorbent to reach equilibrium and changes in its mass.

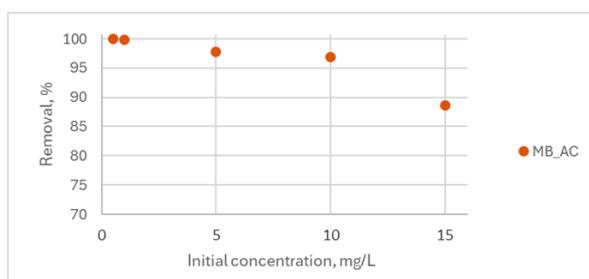


Figure 7. Effect of initial methylene blue (MB) concentration on the date pits activated carbon (DPAC) to remove it from the solution

Table 1. Calculated adsorption masses (q_e) accounting for variations in adsorbent mass and equilibration duration

pH	AC	Time (min)	AC	Initial Concentration	AC
3	2.10	15	3.66	0.5	0.50
4	4.30	30	4.20	1.0	0.99
5	4.88	45	4.25	5.0	4.90
6	4.88	60	4.60	10.0	9.70
7	4.93	90	4.20	15.0	13.30
8	4.94	120	4.18		
9	4.95	180	4.80		

Note: AC: Activated carbon.

This concentration-independent efficacy is rare in adsorption systems, where efficiency generally diminishes with elevated pollutant loads due to site saturation [32]. DPAC durability underscores the elevated concentration of active sites and improved pore structure for the absorption of cationic dyes.

DPAC exhibited remarkable adsorption kinetics for MB, attaining 95% removal in under 15 minutes and nearly complete removal (~100%) by 60 minutes under controlled circumstances (Figure 8). The pseudo-second-order kinetic model (chemisorption) agrees with the isotherm data. The significant correlation observed by the Langmuir/Freundlich models aligns with a chemisorption mechanism, likely involving electrostatic attraction between the negatively charged AC surface (pH 6–9) and the cationic MB dye. This fast absorption surpasses the majority of biomass-derived adsorbents [33] and nears the kinetics of high-performance carbon nanotubes [34].

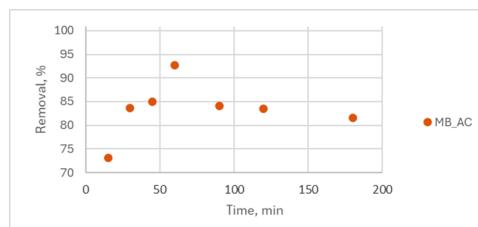


Figure 8. Effect of contact duration on date pits activated carbon (DPAC) to remove methylene blue (MB)

3.3 Sorption Isotherms

The options of the Freundlich and Langmuir isotherm models were justified using static adsorption data. Adsorption isotherm studies of MB on DPAC were investigated using various isotherm models such as, Freundlich and Langmuir. The parameters were calculated and are presented in Figure 9 and Figure 10, where R^2 for the two models studied was found close to identical values ranging from 0.972 to 0.993, indicating a reasonable fit of data for the two models.

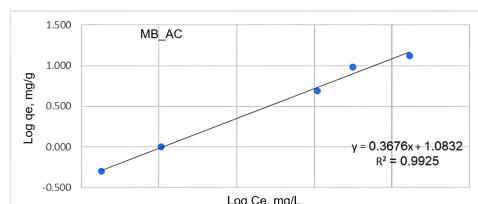


Figure 9. Langmuir isotherms of the adsorption of methylene blue (MB) from aqueous solutions using date pits activated carbon (DPAC) pH 7 and 25 °C

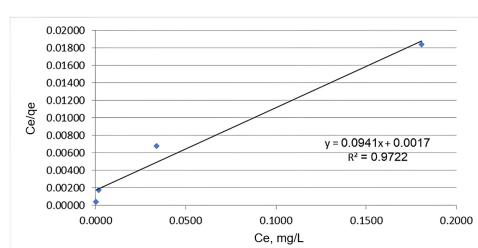


Figure 10. Isotherms of Freundlich methylene blue (MB) adsorption from water-based solutions utilizing date pits activated carbon (DPAC) at pH 7 and 25 °C

The equilibrium isotherm data were similarly fitted to the Langmuir and Freundlich models. The elevated R^2 value (0.9925) for the Langmuir isotherm signifies that the adsorption process mainly supports a monolayer model on a surface with a limited number of equivalent sites.

3.4 Kinetics Studies

The models were employed to assess the adsorption kinetics: The pseudo-first-order model suggests that the rate of adsorption is proportional to the number of available sites, assuming the adsorption occurs on a single site. In contrast, the pseudo-second-order model posits that chemisorption, which involves valence forces or electron sharing, is the rate-limiting step. Figure 11 depicts the intraparticle diffusion model, which investigates how adsorption is impacted by diffusion within the adsorbent pores.

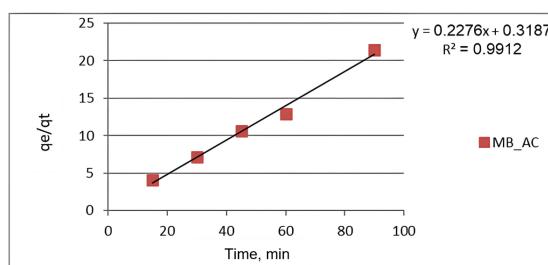


Figure 11. Adsorption kinetics of date pits activated carbon (DPAC)

A strong correlation coefficient ($R^2 = 0.99$) demonstrated that the adsorption process was consistent with the pseudo-second-order model. This suggests that chemisorption is the dominant mechanism, in which strong interactions, such as electrostatic attraction and chemical bonding, occur between the MB molecules and the DBAC surface.

The intraparticle diffusion model showed that adsorption occurred in multiple stages: rapid surface adsorption followed by slower diffusion into micropores. Equilibrium was reached within 60–120 minutes, and the adsorption rate increased with the adsorbent dosage.

These results confirm that the adsorption process is not purely physical, but rather controlled by surface interactions, making DPAC a highly effective adsorbent.

3.5 Thermodynamic Studies of Adsorption

Table 2 lists thermodynamic calculations of MB adsorption. These thermodynamic values were obtained using a data correlation with $R^2 > 0.9958$. Negative and positive ΔG° values mean that ion adsorption on AC was a thermodynamically natural and unnatural process. Additionally, the degree of spontaneity of adsorption of MB rose with temperature. ΔH° values matched an exothermic adsorption for DPAC chemical and physical forces of removal are supposed to be present in that case [35]. Consider that the adsorbate requires thermal energy to navigate the fluid and access the adsorption sites for removal [36]. For MB adsorption, ΔS° for AC was -0.3125 kJ/mol. These negative results indicated lower disorderliness at AC during the dye removal MB [37].

Table 2. Thermodynamic parameters for methylene blue (MB) adsorption on activated carbon (AC) at pH 7

C_0 (mg/L)	C_e (mg/L)	T (K)	K_L	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/K·mol)
5	0.77	298	5.54	-4.24		
	1.82	308	1.75	-1.43	-0.09754	
	3.21	318	0.56	1.53		-0.3125
	4.36	328	0.15	5.23		

A negative ΔG° value (-4.24 kJ/mol at 298 K) confirms that MB adsorption onto DPAC is spontaneous and thermodynamically favorable. The increasing ΔG° values with temperature suggest that adsorption is less favorable at higher temperatures. A negative ΔH° (-0.0975 kJ/mol) suggests an exothermic process, meaning adsorption is driven by heat release and occurs more efficiently at lower temperatures. A negative ΔS° (-0.3125 kJ/mol·K) indicates reduced disorder at the adsorbent-dye interface, suggesting strong interactions between MB molecules and the DPAC surface.

The findings of this study suggest that eco-friendly AC synthesized from date pits can be effectively used as an alternative adsorbent for removing organic dyes from wastewater. This approach holds significant promise for regions with abundant agricultural waste, particularly in arid and semiarid zones. The methodology could be adapted for

other biomass sources, enabling sustainable and low-cost water purification techniques suitable for both industrial and rural settings.

Despite promising results, the study was limited by the use of a single dye MB and laboratory-scale experiments. The adsorbent's performance under real industrial effluent conditions and long-term usage was not evaluated. Additionally, the regeneration and reuse potential of the AC was not explored, which limits insight into its economic viability over time.

Future studies should focus on testing the adsorbent's efficiency on a broader range of organic and inorganic pollutants, including real wastewater samples from various industries. Investigating regeneration techniques and the potential reuse cycles of the AC would provide a clearer understanding of its practical applicability. Furthermore, scaling up the production process and conducting cost-benefit analyses would enhance the feasibility of commercial implementation.

4 Conclusion

AC was synthesized successfully. It effectively removed MB dye from aqueous solutions. DPAC shows a higher proportion of pollutant removal across a wide range of conditions, achieving peak removal (~99%) at pH 6 to 9, a contact period of 60 to 120 minutes, and a sorbent mass of 10 to 60 mg for 10 mL of the dye solution. Characterization by UV-Visible spectroscopy, FTIR, XRD, and SEM elucidated the properties of the produced material. The results were elucidated using the pseudo-second-order kinetic model and the Langmuir isotherm model, and they agree well, with an R^2 value of 0.99. The values of -4.24 kJ/mol, -0.0975 kJ/mol, and -0.3125 kJ/kg/K for ΔG° , ΔH° , and ΔS° indicate that the adsorption of MB is spontaneous, feasible, and exothermic in nature with high intensities at 298 K temperature. In conclusion, utilizing this biosorbent for dye wastewater treatment is an efficient and economical alternative. The synthesis is not only theoretically feasible but also has significant potential for practical, scalable, and cost-efficient applications. Future work should focus on improving the synthesis process to refine DPAC material, analyzing its reusability, and investigating its pollutant removal capabilities.

Author Contributions

Conceptualization, M.F.A. and W.M.S.; methodology, M.F.A. and W.M.S.; validation, M.F.A., W.M.S., and I.A.M.; formal analysis, W.M.S.; investigation, W.M.S. and I.A.M.; resources, N.N.H.; data curation, I.A.M.; writing—original draft preparation, M.F.A. and W.M.S.; writing—review and editing, M.F.A.; visualization, M.I.A. supervision, N.N.H.; project administration, W.M.S. All authors have read and agreed to the published version of the manuscript.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Acknowledgements

The authors thank the Engineering Consulting Office–University of Fallujah, Iraq, for enabling Nahla Naji Hilal to use multiple analytical techniques and instruments in research.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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