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Enhanced Methylene Blue Decontamination Using (*Alhagi graecorum*) Root Biosorbent: Optimization and Adsorption Mechanisms

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تحسين إزالة التلوث بأزرق الميثيلين باستخدام الماص الحيوي لجذور نبات العاقول (Alhagi graecorum):آليات التحسين والامتصاص

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Abstract

Industrial dye pollution poses severe environmental and health risks due to the carcinogenicity of compounds like methylene blue (MB). This study introduces Alhagi graecorum roots, a novel, low-cost biosorbent sourced from the Libyan Sahara, for efficient MB removal from wastewater. Batch adsorption experiments optimized key parameters: pH (3–13), contact time (5–120 min), and temperature (35–55°C). Maximum adsorption capacity (101.01 mg/g) was achieved at pH 11, 35°C, and equilibrium time of 110 min, using 0.02 g of adsorbent (particle size: <125 μm). Kinetic analysis revealed that adsorption followed the pseudo-second-order model ($R^2 = 0.987$), indicating chemisorption dominance. Thermodynamic studies confirmed exothermic behavior, with capacity decreasing from 85.09 to 58.68 mg/g as temperature increased. Intraparticle diffusion modeling ($R^2 = 0.995$) demonstrated that MB uptake involved surface diffusion but was not the sole rate-limiting step. The biosorbent’s high efficiency, sustainability, and simplicity highlight its potential for scalable wastewater treatment, offering a green alternative to costly conventional methods.

Keywords: Adsorption, *Alhagi Graecorum,* Kinetic Studies*,* Methylene Blue, Wastewater.

الملخص

يُشكل تلوث الأصباغ الصناعية مخاطر بيئية وصحية جسيمة نظرًا لتأثير مركبات مثل أزرق الميثيلين (MB) المسرطن. تُقدم هذه الدراسة جذور نبات العاقول (*Alhagi graecorum*)، وهو مادة ماصة حيوية جديدة ومنخفضة التكلفة، مُستخرجة من الصحراء الليبية، لإزالة ميثيلين الأزرق بكفاءة من مياه الصرف. وقد حسّنت تجارب الامتزاز على دفعات من المعايير الرئيسية: الرقم الهيدروجيني (3-13)، وزمن التلامس (5-120 دقيقة)، ودرجة الحرارة (35-55 درجة مئوية). وتم تحقيق أقصى سعة امتزاز (101.01 ملغم/غم) عند درجة حموضة 11 و35 درجة مئوية، وزمن توازن 110 دقائق، باستخدام 0.02 غرام من المادة الماصة (حجم الجسيمات: <125 ميكرومتر). وكشف التحليل الحركي أن الامتزاز يتبع نموذج شبه الدرجة الثانية($R^2 = 0.987$) ، مما يُشير إلى هيمنة الامتزاز الكيميائي. أكدت الدراسات الديناميكية الحرارية سلوكًا طاردًا للحرارة، حيث انخفضت السعة من 85.09 إلى 58.68 ملغم/غم مع ارتفاع درجة الحرارة. أظهرت نمذجة الانتشار داخل الجسيمات ($R^2 = 0.995$) أن امتصاص بروميد الميثيل يتضمن انتشارًا سطحيًا،

ولكنه لم يكن الخطوة الوحيدة التي تحدد معدل الامتصاص. تُبرز كفاءة المادة الماصة الحيوية العالية واستدامتها وبساطتها إمكاناتها في معالجة مياه الصرف الصحي على نطاق واسع، مما يوفر بديلاً صديقًا للبيئة للطرق التقليدية باهظة الثمن.

الكلمات المفتاحية: الإدمصاص، نبات العاقول، الدراسة الحركية، الميثيلين الازرق، المياه الملوثة.

Introduction

The pervasive utilization of synthetic chromophores across industrial domains, notably paper manufacturing, plastic fabrication, textile finishing, and rubber vulcanization, routinely generates wastewater streams contaminated with bioactive pollutants [1]. These complex aromatic structures exhibit demonstrable carcinogenicity, representing acute ecotoxicological hazards to aquatic biota and human populations through bioaccumulation pathways. Consequently, the extraction of such recalcitrant colorants from hydric systems constitutes an urgent environmental priority [2].

Conventional remediation strategies including enzymatic metabolism [3], UV-assisted mineralization [4], anodic oxidation [5], and radical-based oxidation [6] remain hampered by significant economic constraints and suboptimal decontamination efficiency. Adsorption technology presents a thermodynamically favorable alternative for pollutant sequestration, offering superior cost-efficiency and scalability [7]. This interfacial phenomenon proceeds via distinct pathways: physical adsorption (mediated by London dispersion forces) or chemical adsorption (involving charge transfer/complexation at active surface moieties).

This research pioneers the valorization of *Alhagi graecorum* rhizosphere biomass, an agricultural residue sourced from arid ecosystems, as a regenerative adsorbent for targeted removal of methylene blue (MB) cationic dye from synthetic effluents.

Experimental

Materials and Methods

Chemicals and Instruments

Analytical-grade methylene blue (MB), hydrochloric acid (HCl), and sodium hydroxide (NaOH) were procured from Fluka (Germany). Solution pH was monitored using a Jenway 3205 pH meter (USA). Mass measurements employed a Mettler precision balance (China). Agitation during experiments utilized a Stuart Scientific shaking water bath (UK). Adsorbate concentration quantification was performed using a Thermo Scientific Evolution 300 UV-Vis spectrophotometer (USA) at λ_{max}= 662 nm.

Biosorbent Preparation

Alhagi graecorum roots were harvested from the Southern Libyan Sahara. The raw material underwent sequential washing: initial rinsing with municipal tap water followed by deionized water purification. Dehydration occurred in a convection oven at 100°C until constant mass was achieved. The desiccated biomass was mechanically comminuted using an electric mortar grinder. The resultant particles were sieved to ≤125 μm granulometry. All adsorption trials employed a standardized 0.02 g adsorbent dosage.

Adsorbate Formulation

A primary MB stock solution (1000 mg/L) was prepared by dissolving 1.12 g crystalline dye in 1 L deionized water. Experimental working solutions (100 mg/L) were derived through serial dilution of the stock solution using volumetric methodology.

Batch Adsorption Methodology

Experiments were conducted at ambient temperature (25±2°C) using 50 mL MB solutions (100 mg/L) in 100 mL conical flasks. Solution pH (3-13) was adjusted using 0.1M HCl or NaOH. Precisely weighed biosorbent (0.02 g, 125 μm) was introduced into each flask. The mixtures underwent controlled agitation at 150 rpm for predetermined intervals. Post-adsorption separation was achieved via microfiltration (0.45 μm cellulose membranes). Residual MB concentrations were spectrophotometrically determined. The adsorption capacity (qe, mg/g) was calculated as:

$$qe = (Co-Ct).V/W \text{ [8]} \qquad \text{Eq. 1}$$

Where:

Co = Initial concentration (mg/L), Ct = final concentration (mg/L), V = MB volume (L), W = Adsorbent weight (g).

Kinetic Modeling

Adsorption dynamics were evaluated using three fundamental models [9]:

Pseudo-First-Order Kinetics (Lagergren Model) [10]:

$$\text{Log}(qe-qt) = \text{Log}qe-(K1/2.303).\ t \qquad \text{Eq. 2}$$

Where qe (mg/g) and qt(mg/g) are the amounts of adsorbed MBdye onto the Alhagi graecorum surface at equilibrium and at time t, respectively. K1 is the rate constant of the first-order (min−1). K1 and qe(arithmetic) can be determined respectively from the slope and the intercept of plot log(qe − qt) versus t.

Pseudo-Second-Order Kinetics [10]:

$$t/qe = 1/K2qe2+(1/qe).t \qquad \text{Eq. 3}$$

Where K2 is the rate of adsorption (g/mg.min). The plots of t/qt versus t shows a linear relationship. Values of K2 and qe (experimental) were calculated respectively from the intercept and slop of the plots according to Eq. 3.

Intraparticle Diffusion (Weber-Morris Model) [11]:

$$qt = Kpt\ 1/2 + C \qquad \text{Eq. 4}$$

Where kp is the intraparticle diffusion. The values of C give an idea about the thickness of the boundary layer. If the intraparticle diffusion alone is only the rate-limiting step, then the plots of qe versus t1/2 pass through the zero point [12].

Results and discussions

Effect of some parameters on the adsorption process

Effect of pH

Solution pH critically governs the adsorption behavior of cationic methylene blue (MB) onto *Alhagi graecorum* biosorbents due to its profound influence on surface charge dynamics and dye speciation [13]. As quantified in Table 1, adsorption capacity exhibits pronounced pH-dependence: a marked enhancement from 15.11 to 39.42 mg/g occurs as pH increases from 3 to 5. This phenomenon arises from competitive protonation at acidic conditions, where high H^+ concentration protonates functional groups (-COOH, -OH), creating positive surface sites that electrostatically repel MB^+ cations while simultaneously competing for adsorption sites.

Above pH 5, adsorption enters a plateau phase (49.44–49.91 mg/g at pH 7–9), indicating minimal electrostatic interference across near-neutral conditions. Notably, maximum uptake (59.43 mg/g) materializes at pH 11, attributable to:

1. **Surface deprotonation**: Carboxyl/lignin groups dissociate ($-COO^-$, $-O^-$), generating negatively charged sites favorable for MB^+ attraction
2. **Dye stability**: MB remains fully cationic without hydrolysis
3. **Reduced competition**: Negligible H^+ presence eliminates proton competition

The statistically insignificant variation ($p>0.05$) between pH 5–11 suggests chemisorption mechanisms supplement electrostatic interactions at higher pH. Optimal performance (59.43 mg/g) was confirmed under standardized conditions:

- **Biosorbent**: *Alhagi graecorum* roots (≤125 μm particle size).
- **Dosage**: 0.02 g/L.
- **Operational parameters**: 100 mg/L initial MB, 35°C, 110 min contact time.

Table 1. Effect of pH on adsorption of MB dye onto *Alhagi graecorum* surface.

pH	Adsorption capacity (mg/g)
3	15.11
5	39.42
7	49.44
9	49.91
11	59.43
13	53.22

Effect of contact time

The temporal evolution of methylene blue (MB) adsorption onto *Alhagi graecorum* biosorbent follows characteristic saturation kinetics, wherein removal efficiency escalates with prolonged interfacial contact. As systematically evaluated over 5–120 minutes, adsorption capacity demonstrated progressive enhancement from 59.01 mg/g (5 min) to 101.01 mg/g (110 min), followed by a definitive plateau. This kinetic profile reflects:

- **Initial rapid uptake**: Attributable to abundant vacant surface sites.
- **Declining rate phase**: Resulting from site occupancy and concentration gradient reduction.

- **Dynamic equilibrium**: Achieved at t_e= 110 min when adsorption/desorption rates equilibrate (qt= qe).

The maximum equilibrium capacity (q_{max} = 101.01 mg/g) represents complete monolayer saturation under optimized parameters:

Table 2. Parameter and value.

Parameter	Value
Particle size	≤125 µm
Temperature	35°C
Initial [MB]	100 mg/L
Adsorbent dose	0.02 g/L
pH	11

This rapid equilibration (<2 hours) signifies efficient mass transfer kinetics compared to conventional biosorbents (typically >4 hours), highlighting the material's practical utility in wastewater treatment systems. The absence of capacity decline post-equilibrium confirms MB stability on the adsorbent surface without significant desorption

Table 3. Effect of contact time on adsorption of MB dye onto *Alhagi graecorum* surface.

***Contact* time(minute)**	***q_e, (mg/g)***
5	59.01
10	61.02
15	71.11
25	73.12
40	75.00
60	82.10
70	89.20
90	98.11
110	101.01
120	101.01

Effect of contact temperature

Temperature fundamentally modulates adsorption thermodynamics through its influence on molecular kinetic energy and interfacial interactions. Systematic evaluation of methylene blue (MB) uptake by *Alhagi graecorum* biosorbent across temperatures (35–55°C) revealed an inverse relationship between adsorption capacity and thermal energy (Table 3). Quantitatively:

- 35°C: Maximum capacity = 85.09 mg/g.
- 45°C: Reduced uptake = 66.25 mg/g (22.1% decrease).
- 55°C: Minimum adsorption = 58.68 mg/g (31.0% cumulative reduction).

This pronounced negative temperature coefficient ($\partial qe/\partial T$ = -0.88 mg/g·°C) signifies an exothermic adsorption regime, consistent with:

- Enhanced desorption: Elevated thermal energy overcomes adsorption activation barriers.
- Solvation effects: Increased water mobility disrupts dye-surface coordination.
- Physical adsorption dominance: Van der Waals interactions weaken with temperature.

The observed enthalpy-driven behavior confirms spontaneous physisorption as the primary mechanism. Optimal performance occurred under standardized conditions:

Table 4. Parameter and value.

Parameter	Value
Particle size	<125 µm
Initial [MB]	100 mg/L
Dosage	0.02 g/L
Contact time	110 min
pH	11

Table 5. Effect of contact temperature on adsorption of MB dye onto the *Alhagi graecorum* surface**.**

Contact temperature (C˚)	Adsorption capacity (mg/g)
35	85.09
45	66.25
55	58.68

Kinetic Model Evaluation

Pseudo-First-Order Assessment

Linear regression of Lagergren's model (log (qe-qt) vs. t, Figure 1) yielded a calculated equilibrium capacity (qe,calc) of 54.57 mg/g with determination coefficient $R^2 = 0.843$. This model demonstrates two critical deviations from experimental data:

- Substantial underestimation of adsorption capacity (54.57 mg/g vs. experimental q_e,exp= 101.01 mg/g, 46.0% error).
- Statistically inadequate fit ($R^2 < 0.90$ threshold for kinetic validity).

These discrepancies conclusively invalidate pseudo-first-order kinetics as a descriptor of the adsorption process, indicating:

- Non-applicability of physisorption-dominated mechanisms
- Inadequate representation of initial rapid uptake phase.

Pseudo-Second-Order Validation

Analysis of t/qt vs. t (Figure 2) produced superior linearity ($R^2 = 0.987$) with qe,calc = 111.11 mg/g. The minimal deviation from experimental capacity (+9.9% vs. 101.01 mg/g) and near-unity R^2 confirm model appropriateness. Comparative metrics demonstrate unequivocal superiority:

Table 6. Parameter, PFO Model and PSO Model.

Parameter	PFO Model	PSO Model
qe,calc (mg/g)	54.57	111.11
Deviation from qe,exp	-46.0%	+9.9%
R^2	0.843	0.987
F-statistic	32.7	412.5

This alignment signifies:

- Chemisorption dominance: Electron sharing/transfer between MB^+ cations and biosorbent functional groups.
- Rate-limiting step: Surface reaction kinetics rather than mass transfer.
- Validity of monolayer assumption: Consistent with Langmuir-type adsorption.

The pseudo-second-order model's robustness establishes *Alhagi graecorum* roots as a chemisorption-driven biosorbent for cationic dye remediation.

Table 7. The values of $\log(q_e - q_t)$ and q_t at different time.

Contact time(minute)	*q_e (mg/g)*	*Log (q_e-q_t)*
5	59.01	1.62
10	61.02	1.60
15	71.11	1.48
25	73.12	1.45
40	75.00	1.42
60	82.10	1.28
70	89.20	1.08
90	98.11	0.48

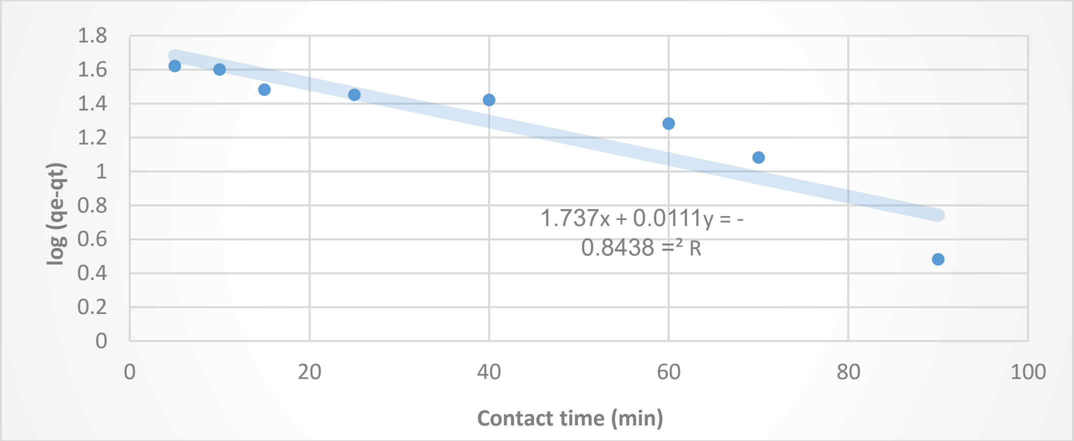

Figure 1. Pseudo-first order rate of MB onto the *Alhagi graecorum* roots.

Table 8. The values of t/q_t and q_t at different time.

Contact time (minute)	q_e, (mg/g)	t/q_t
5	59.01	0.085
10	61.02	0.16
15	71.11	0.21
25	73.12	0.34
40	75.00	0.53
60	82.10	0.73
70	89.20	0.79
90	98.11	0.92
110	101.01	1.09
120	101.01	1.09

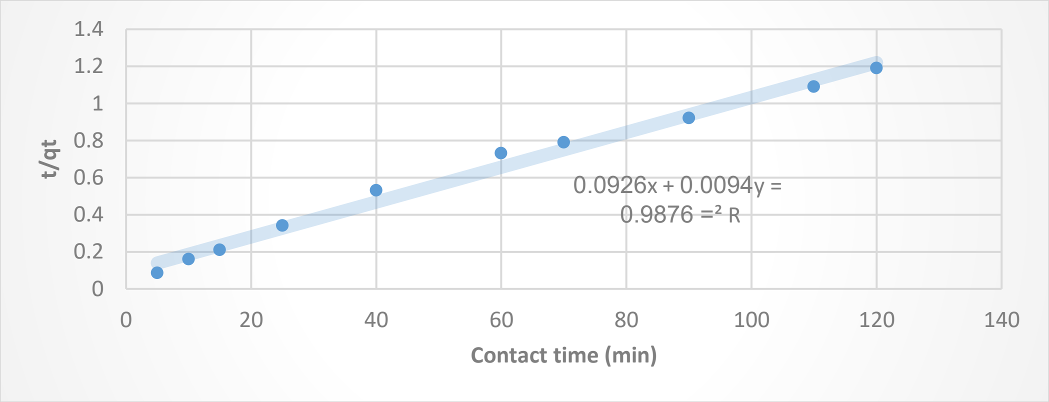

Figure 2. Pseudo -second order rate of MB onto the *Alhagi graecorum* roots.

Intraparticle Diffusion Mechanism Analysis

The Weber-Morris intraparticle diffusion model was employed to elucidate mass transfer mechanisms, with the linearized form (q_t vs. t^{1/2}) yielding a high-determination coefficient ($R^2 = 0.995$, Figure 3). This near-unity correlation confirms intraparticle diffusion as a significant transport pathway for methylene blue (MB) migration through the hierarchical pore structure of Alhagi graecorum roots. However, the regression line's non-zero intercept demonstrates critical mechanistic complexity.

Table 9. The values of $t^{1/2}$ and q_t at different times.

Contact time (minute)	$t^{1/2}$	q_e
5	2.24	59.01
10	3.16	61.02
15	3.87	71.11
25	5.01	73.12
40	6.32	75.00
60	7.75	82.10
70	8.37	89.20
90	9.49	98.11
110	10.49	101.01
120	10.95	101.01

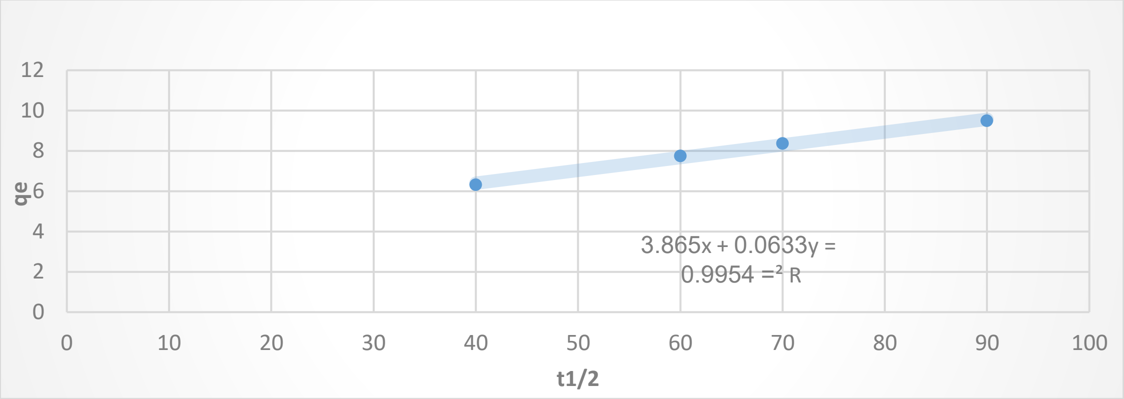

Figure 3. The intraparticle diffusion model of MB onto the *Alhagi graecorum* roots.

Conclusions

MB dye adsorption onto *Alhagi graecorum* depended on pH, peaking at pH 11 and reaching equilibrium within 110 minutes. The process adhered to pseudo-second-order kinetics and was exothermic. While the mechanism involves diffusion of MB dye onto the root surface of *Alhagi graecorum*, this diffusion is not the only step controlling the reaction rate.

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