Vu thanh

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Vật Liệu Composite Có Nguồn Gốc Phụ Phẩm Hấp Phụ Methylene Blue Trong Dung Dịch: Nghiên Cứu Động Học, Đẳng Nhiệt và Nhiệt Động Lực Học Hấp Phụ

TÓM TẮT

Vật liệu hấp phụ composite (ACPU) đã được tổng hợp từ than hoạt tính có nguồn gốc từ bã cà phê đã qua sử dụng, chitosan, polyvinyl alcohol (PVA) và nhựa polyester không bão hòa (UPE), với glutaraldehyde đóng vai trò chất tạo liên kết ngang. Quá trình đặc trưng hóa bằng FT-IR, BET và SEM xác nhận sự tích hợp thành công của các thành phần và sự hình thành liên kết Schiff base (C=N), cho thấy sự tạo thành liên kết hình thành nên cấu trúc vật liệu. Vật liệu composite cho thấy cấu trúc mao quản trung bình với đường kính lỗ trung bình là 21,1 Å và diện tích bề mặt đạt 13,320 m^2/g. Hình ảnh SEM cho thấy bề mặt thô không đồng nhất, thuận lợi cho quá trình hấp phụ. Khả năng hấp phụ methylene blue (MB) đã được đánh giá dưới các điều kiện khác nhau. Khả năng hấp phụ tối ưu được ghi nhận trong môi trường kiềm, với dung lượng hấp phụ cực đại đạt 295,09 mg/g tại nồng độ MB 40 mg/L. Dữ liệu động học phù hợp với mô hình giả bậc hai ($R^2 > 0,99$), trong khi các mô hình đẳng nhiệt Freundlich và Dubinin-Radushkevich mô tả tốt dữ liệu cân bằng, cho thấy cơ chế hấp phụ vật lý đa lớp. Phân tích nhiệt động học cho thấy quá trình hấp phụ diễn ra một cách tự phát và tỏa nhiệt ($\Delta H° = -98,36$ kJ/mol, $\Delta G° < 0$), kèm theo sự giảm entropy tại bề mặt pha rắn–lỏng. Kết quả này cho thấy tiềm năng ứng dụng của vật liệu composite có nguồn gốc từ phụ phẩm như một chất hấp phụ hiệu quả,chi phí thấp và thân thiện với môi trường trong xử lý nước thải chứa thuốc nhuộm.

Từ khoá: *Chất hấp phụ composite, Đẳng nhiệt, Động học, Nhiệt động lực học, Xanh Methylene*.

A Bio-Waste Derived Composite Adsorbent for Methylene Blue Adsorption from Aqueous Solution: A Study on Kinetics, Isotherms and Thermodynamics

ABSTRACT

A composite adsorbent (ACPU) was synthesized using activated carbon derived from spent coffee grounds, chitosan, polyvinyl alcohol (PVA), and unsaturated polyester resin (UPE), with glutaraldehyde serving as a crosslinking agent. Comprehensive characterization by FT-IR, BET, and SEM confirmed the successful integration of components and the formation of Schiff base (C=N) linkages, indicating effective chemical bonding. The composite exhibited a mesoporous structure (average pore diameter: 21.1 Å; surface area: 13.320 m^2/g), and SEM analysis revealed a rough, heterogeneous surface favorable for adsorption. The adsorption performance of methylene blue (MB) was evaluated under varying operational parameters. Optimal adsorption was observed at alkaline pH, with maximum uptake of 295.09 mg/g at 40 mg/L MB concentration. Kinetic data fitted the pseudo-second-order model ($R^2 > 0.99$), while the Freundlich and Dubinin-Radushkevich isotherms provided the best description of the equilibrium data, indicating favorable multilayer physical adsorption. Thermodynamic analysis revealed spontaneous and exothermic behavior ($\Delta H° = -98.36$ kJ/mol, $\Delta G° < 0$), with reduced entropy at the solid liquid interface. These results underscore the potential of this bio-waste-derived composite as an efficient, low cost, and environmentally friendly adsorbent for dye-contaminated wastewater treatment.

Keywords: *Composite Adsorbent, Isotherms, Kinetics, Methylene Blue, Thermodynamics*.

1. INTRODUCTION

In contemporary society, water pollution has emerged as a pressing global concern, particularly within the textile industry—recognized as one of the primary contributors to environmental degradation due to the release of hazardous substances such as heavy metals, synthetic dyes, and high alkaline effluents.[1] Among these pollutants, methylene blue (MB), a cationic dye extensively utilized in textile processing, poses significant ecological and health risks owing to its chemically stable structure, resistance to biodegradation, and toxicity to both humans and aquatic life. Exposure to MB has been associated with adverse effects including ocular irritation, gastrointestinal disturbances (e.g., vomiting, diarrhea), and potential mutagenic and carcinogenic consequences.[1]

Conventional wastewater treatment methods such as coagulation–flocculation and redox-based processes have been widely implemented; however, these techniques often suffer from drawbacks including high operational costs, substantial energy requirements, and the generation of harmful secondary by-products.[2] In contrast, adsorption has gained considerable attention as an efficient, straightforward, and environmentally benign approach for the removal of dyes from aqueous systems, as it minimizes the formation of secondary pollutants.[3]

Recent research has increasingly focused on the utilization of carbonaceous bio-sorbents derived from agricultural waste materials, owing to their abundance, low cost, and environmental sustainability.[4] Despite these advantages, challenges remain regarding the separation and regeneration of such bio-sorbents after use, which hinders their practical application on an industrial scale. As a result, the development of reusable and easily recoverable bio-sorbents has become a critical area of interest.

One of the early reports of using magnetic cellulose beads, combining magnetic particles with cellulose and activated carbon for removing MB in aqueous solution showed that adsorption capacity is 2.13×10^{-3} mmol/g and these beads can be reused for 3 times.[5] However, the preparation process is so complicated and requires a special piece of equipment (submerged circulative impinging stream reactor). A similar study was conducted using magadiite/chitosan composite beads for adsorption Methylene Blue with adsorption capacity of 45.25 mg/g.[6] Besides cellulose, chitosan and alginate in form of hydrogels or beads showed their ability to remove azo dyes from aqueous solution.[7,8] Therefore, it is able to use a composite bead consisting of Activated carbon, Chitosan, PVA, and UPE to remove dyes from aqueous solution.

Previous studies have explored magnetic cellulose-based beads composed of magnetic particles, cellulose, and activated carbon for MB adsorption, reporting a maximum capacity of 2.13×10^{-3} mmol/g and reusability up to three cycles.[5] However, their synthesis involves complex procedures and requires specialized equipment such as a submerged circulative impinging stream reactor. Similar efforts using magadiite/chitosan composite beads have achieved higher adsorption capacities (e.g., 45.25 mg/g),[6] while other natural polymers such as chitosan and alginate—typically in hydrogel or bead form—have demonstrated effectiveness in azo dye removal from aqueous solutions.[7,8]

Building upon these findings, the present study reports the synthesis and performance evaluation of a novel composite bead adsorbent formulated from activated carbon derived from spent coffee grounds, chitosan, polyvinyl alcohol (PVA), and unsaturated polyester resin (UPE). The adsorption characteristics of the resulting composite material (denoted as ACPU) toward methylene blue were systematically examined under varying experimental conditions, including pH, contact time, initial dye concentration, and temperature. To elucidate the underlying adsorption mechanisms, kinetic modeling, equilibrium isotherm analysis, and thermodynamic assessments were performed. This study aims to propose a cost-effective, sustainable, and easily separable adsorbent with high potential for practical application in dye-laden wastewater treatment under ambient conditions.

2. Material and Methods

2.1. Material

Chitosan, possessing a degree of deacetylation exceeding 80% and a molecular weight of 87 kDa, was obtained from S-Green Company (Vietnam). Methylene blue dye (purity ≥ 99%) was purchased from Xilong Chemical Co., Ltd. (China). Other chemicals used in the study included glacial acetic acid (≥ 99.5%), hydrochloric acid (36–38%), sodium hydroxide (≥ 98%), and glutaraldehyde solution (37%). Polyvinyl alcohol (PVA) and unsaturated polyester resin (UPE) were also sourced from Xilong Chemical.

2.2. Preparation of Bio-Waste Derived ACPU Composite Adsorbent

Activated carbon was prepared based on the method described by Giraldo et al. (2012), with minor modifications to accommodate the specific experimental parameters of this study.[9] Spent coffee grounds were collected, thoroughly rinsed with distilled water to remove surface contaminants, and subsequently dried at 60 °C. The dried biomass was then subjected to carbonization in a muffle furnace at 850 °C for 1 h. The resulting char was chemically activated by soaking in 1 M phosphoric acid (H_3PO_4) at a solid-to-liquid ratio of 1:10 (w/v) for 2 h at room temperature to enhance surface area and porosity. After activation, the material was repeatedly washed with distilled water under ultrasonic agitation until the filtrate reached a neutral pH. The activated carbon (AC) was then oven-dried, pulverized, and sieved to obtain a fine powder suitable for use in composite adsorbent formulation. This process effectively converts agricultural waste into a functional material for environmental remediation.

In accordance with the procedure outlined by Nowruzi et al. (2020), the composite adsorbent was synthesized using AC, chitosan, polyvinyl alcohol (PVA), and unsaturated polyester (UPE) under alkaline conditions at ambient temperature.[10] Specifically, 4 g of AC was dispersed in 100 mL of distilled water using ultrasonic treatment for 10 min at a frequency of 40 kHz and power of 100 W. In parallel, 4 g of chitosan was dissolved in 100 mL of 1% (v/v) acetic acid with continuous stirring at 65 °C for 2 h to obtain solution A. For solution B, 4 g of PVA was added to 100 mL of deionized water and heated at 90 °C for 5 h until complete dissolution. Solution C was prepared by dissolving 4 g of UPE in 100 mL of deionized water. The three solutions were then combined and stirred at 90 °C for 1 h to form a homogeneous mixture. The resulting mixture was dropwise introduced into a 0.25 M sodium hydroxide solution and allowed to solidify for 2 h. The formed composite beads were subsequently washed with distilled water until neutral pH was achieved. Crosslinking was carried out by immersing the beads in 25% (v/v) glutaraldehyde solution under stirring for 2 h. The final ACPU composite granular adsorbents were collected using a Whatman membrane filter, washed thoroughly with distilled water, and dried in a vacuum oven (Memmert VO101) at 60 °C and 0.6 bar pressure for 6 h.

2.3. Adsorption of Methylene Blue onto the Composite Adsorbent

To evaluate the adsorption performance of the synthesized composite adsorbent, batch experiments were conducted using MB solutions prepared by diluting a 100 mg/L stock solution with deionized water to obtain the required concentrations. The adsorption studies were carried out on a Digisystem orbital shaker (model OS350D) operating at 150 rpm. A systematic investigation was performed to examine the effects of critical operational parameters, including solution pH, initial dye concentration, contact time, adsorbent dosage, and temperature, employing a univariate experimental design. The concentration of MB in solution before and after reaching adsorption equilibrium was determined by measuring absorbance at $\lambda_{max} = 665$ nm using a UV–Vis spectrophotometer (Labomed UVD-3500), with reference to a pre-established calibration curve. The adsorption capacity of the ACPU composite was subsequently calculated using conventional adsorption equations.

$$q = \frac{(C_o - C_e).V}{m} \qquad (1)$$

where, C_o (mg/L) is the initial concentration and C_e (mg/L) is the concentration at equilibrium. V (L) is the volume of the solution and m (g) is the mass of the adsorbent.

The point of zero charge (pH_{pzc}) of the composite adsorbent was determined to assess its surface charge properties under different pH conditions. For this purpose, 0.1 g of the adsorbent was added to 25 mL of a 0.1 M KCl solution in a 250 mL Erlenmeyer flask. The initial pH of the suspension was adjusted within the range of 2 to 12 using either 0.1 M NaOH or 0.1 M HCl. The mixtures were agitated and allowed to equilibrate for 24 h. Subsequently, the final pH of each suspension was measured. The pH_{pzc} was identified as the pH at which the difference between the initial and final pH values (ΔpH) was zero. This analysis offers valuable information regarding the surface charge behavior of the adsorbent and its interaction potential with ionic species in aqueous media.[10]

To gain deeper insight into the adsorption mechanism, rate-controlling steps, and thermodynamic characteristics of the process, various kinetic, isotherm, and thermodynamic models were employed. The pseudo-first-order (PFO) model was applied to describe the nonlinear relationship between the occupancy of adsorption sites and the rates of adsorption and desorption. In contrast, the pseudo-second-order (PSO) model assumes a linear correlation between the square of site occupancy and the adsorption rate, providing a different perspective on the adsorption kinetics. Additionally, the intraparticle diffusion model was utilized to investigate the contribution of internal diffusion to the overall adsorption mechanism of methylene blue onto the composite adsorbent.[11]

$$q_t = q_e(1 - e^{-k_1 t}) \qquad (2)$$

$$q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t} \qquad (3)$$

$$q_{ref} = k_p t_{ref}^{1/2} + C \qquad (4)$$

$$\left(\frac{q_t}{q_{ref}}\right) = 1 - R_i\left[1 - \left(\frac{t}{t_{ref}}\right)^{1/2}\right] \qquad (5)$$

where, k_1 (1/min) is the PFO rate constant, k_2 (g/mg.min) represents a PSO rate constant, k_p (mg/g.min$^{1/2}$) is the intra-granular diffusion constant.

Adsorption isotherms are employed to elucidate the interaction behavior between MB and the ACPU composite beads at equilibrium. Among the most commonly utilized models are the Langmuir and Freundlich isotherms. The Langmuir model assumes monolayer adsorption onto a homogeneous surface with uniform adsorption sites, where no interactions occur between adsorbed molecules and no chemical reactions take place. In contrast, the Freundlich model accounts for multilayer adsorption on a heterogeneous surface with varying affinities. Additionally, the Dubinin–Radushkevich (D–R) isotherm model is applied to distinguish between physical and chemical adsorption mechanisms. According to this model, a mean free energy (E) value below 8.0 kJ/mol indicates a physical adsorption process, while values exceeding 8.0 kJ/mol are characteristic of chemisorption.[11]

Langmuir isotherms:

$$q_e = q_{max}\frac{k_L - C_e}{1 + k_L - C_e} \qquad (6)$$

where, q_e (mg/g) is the amount of adsorbate adsorbed per mass of adsorbent; C_e (mg/L) is the equilibrium concentration of the adsorbate; q_{max} (mg/g) and K_L (L/mg) are Langmuir characteristic constants indicating maximum adsorption capacity and the energy of adsorption, respectively.

Freundlich isotherms:

$$q_e = k_F.C_e^{1/n} \qquad (7)$$

where, q_e (mg/g) is the amount of adsorbate adsorbed per mass of adsorbent; C_e (mg/L) is the adsorbate equilibrium concentration; K_F (mg/g) and 1/n are Freundlich characteristic constants representing adsorption capacity and adsorption intensity, respectively

Dubinin–Radushkevich (D–R) isotherms:

$$\ln q_e = \ln q_m - \beta . \varepsilon^2 \tag{8}$$

where q_e is the amount of the dye adsorbed per mass of the adsorbent in (mg/g), β is a constant related to the mean free energy of adsorption per mole of the adsorbate (mol^2/J^2), ε is the Polanyi potential calculated from the equation

Thermodynamic analysis, commonly based on the Van't Hoff equation, yields key parameters including Gibbs free energy change (ΔG°), enthalpy change (ΔH°), and entropy change (ΔS°), thereby offering valuable insights into the feasibility, spontaneity, and energetic nature of the adsorption process.

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \tag{9}$$

$$\ln K_C = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R} \tag{10}$$

where, T (K) and R (8.314 J/mol.K) are the absolute temperature and universal gas constant, respectively. K_C is the constant of equilibrium. The above-mentioned parameters are obtained by drawing a fitted linear line graph of ln K_C relative to 1/T. C_0 and C_e are initial and final concentration of MB (mg/L), respectively.

2.4. Physicochemical properties of adsorbent

To examine the functional group transformations of the composite beads, Fourier-transform infrared (FT-IR) spectroscopy was performed using a NICOLET 6700 spectrophotometer (Thermo), covering the spectral range of 4000–400 cm^{-1}. The surface morphology of the composite material was characterized by scanning electron microscopy (SEM) using an instrument manufactured by Horiba. The specific surface area and pore characteristics of the composite adsorbent were determined via the Brunauer–Emmett–Teller (BET) method, based on nitrogen adsorption–desorption isotherms measured over a relative pressure (P/P_0) range of 0.05 to 1.0. Pore size distribution and volume were further analyzed using the density functional theory (DFT) model with a Nova 1000e surface area analyzer (Quantachrome).

3. RESULT AND DISCUSSION

3.1. Physicochemical properties of adsorbent

The formation of new chemical interactions within the ACPU composite is evidenced by the appearance and shifts of characteristic FT-IR absorption bands compared to those of the individual components (Figure 1A). In particular, the emergence of a prominent band at 1730 cm^{-1}, corresponding to the C=O stretching vibration of ester groups, confirms the successful incorporation of unsaturated polyester resin (UPE) into the polymeric matrix. This absorption peak, which is absent or negligible in pure chitosan (CS) and PVA spectra, suggests potential esterification reactions or strengthened hydrogen bonding between the carboxyl and ester functionalities of UPE and the hydroxyl groups present in PVA and chitosan.[10],[12]

Moreover, the broadening and slight shift of the –OH and –NH stretching vibration band around 3350 cm^{-1} to a wider range spanning 3300–3400 cm^{-1} indicates the establishment of intermolecular hydrogen bonds among the hydroxyl and amine groups of CS, PVA, and surface functional groups on AC.[10] The band observed near 2930 cm^{-1} is assigned to the symmetric and asymmetric stretching modes of aliphatic C–H bonds, confirming the presence of organic backbones from CS, PVA, and UPE. These interactions collectively enhance the structural integrity of the composite.[12] Similarly, shifts detected in the C–O–C stretching region near 1080 cm^{-1} imply the possible formation of new hydrogen-bonded or covalently linked C–O–C bridges among the polymer components.[13]

Additionally, the appearance of a band at approximately 1650 cm^{-1}, attributed to the stretching vibration of imine (C=N) groups, provides strong evidence of Schiff base formation within the composite network. Concurrently, a notable decrease in intensity of the amide II band around 1560 cm^{-1}—corresponding to N–H bending and C–N stretching vibrations of free amine groups in chitosan—suggests their involvement in the crosslinking reactions.[13] Collectively, these spectral modifications substantiate the creation of a novel composite framework, stabilized by a combination of hydrogen bonding and probable esterification. The integration of these interactions results in a structurally cohesive material with improved adsorption performance.

BET analysis (Figure 1B) revealed that the specific surface area of the composite particles was 13.320 m^2/g, which is lower than that of the AC alone. This reduction is likely attributable to the crosslinking interactions among AC, CS, and glutaraldehyde. The N_2 adsorption–desorption isotherm exhibited a type V profile, with an average pore diameter of

21.104 Å, indicating a mesoporous structure characterized by slit-shaped pores and relatively weak interactions between the adsorbate and adsorbent. These findings align with observations from scanning electron microscopy (SEM). The composite exhibited a high mesoporosity degree of 97.88%, favoring the adsorption of MB, whose molecular dimensions are approximately 14.2 Å × 9.5 Å.[14] Consequently, MB adsorption predominantly occurs through weak physical interactions within the composite matrix.

The surface morphology of the synthesized ACPU composite was investigated by SEM at magnifications of 1,000× and 10,000× (Figure 1C). At 1,000× magnification, the composite displayed a heterogeneous and highly textured surface comprising irregular fragments, layered folds, and interconnected microstructures. Such morphology reflects a multi-component system wherein activated carbon particles are embedded within a polymeric matrix composed of CS, PVA, and UPE. The observed rough and wrinkled surface topology, along with visible microvoids and cracks, may be attributed to rapid polymer solidification and phase incompatibility during the crosslinking process.[15] These structural characteristics enhance surface area and facilitate the diffusion of adsorbate molecules, thereby benefiting adsorption performance.

At higher magnification (10,000×), the composite surface exhibited smoother polymeric regions interspersed with discontinuous phases and microporous domains. The presence of fine cracks and lamellar textures was noted, while the absence of large phase-separated domains suggests that glutaraldehyde crosslinking and hydrogen bonding interactions—particularly between hydroxyl (–OH) and amine ($-NH_2$) groups—promote a relatively homogeneous composite microstructure.[16] The intimate interfacial contact among components further indicates good compatibility and successful integration of bio-based and synthetic constituents.[15]

These SEM observations corroborate the proposed mechanism of composite formation, wherein AC serves as a porous adsorption backbone, CS and PVA provide hydrophilic functional groups, and UPE contributes to mechanical stability. The resultant micro-structure offers high surface accessibility and internal porosity, both critical for the effective adsorption of contaminants such as MB.

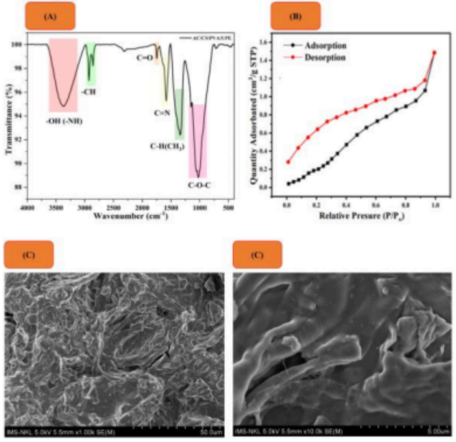


Figure1. Physicochemical properties of adsorbent FT-IR (A), adsorption/desorption N_2 (B), and x1,000 and x10,000 (C).

3.2. Adsorption of MB onto the ACPU Adsorbent

The adsorption capacity of MB onto ACPU composite particles is influenced by several key parameters, as illustrated in Figure 2. As the solution pH increases from 4 to 6, the adsorption capacity exhibits a modest rise from 67.15±0.02 mg/g to 70.86±0.05 mg/g, followed by a further increase to approximately 77.50±0.02 mg/g within the pH range of 9–10 (Figure 2A). This trend can be attributed to alterations in the adsorbent's surface charge and the deprotonation occurring at higher pH values, which enhance the electrostatic attraction between the negatively charged adsorbent surface and the cationic MB molecules.[17]

The effect of contact time on MB adsorption is depicted in Figure 2B, demonstrating a rapid increase in adsorption capacity from 22.53±0.04 mg/g at 0.5 h to 73.23±0.03 mg/g after 4 h, followed by a gradual approach to equilibrium, reaching about 76.64±0.03 mg/g at 24 h. This behavior is explained by the initial rapid adsorption of MB onto readily accessible active sites on the particle surface, succeeded by slower intraparticle diffusion of dye molecules into the interior of the granular adsorbent.[17] The reduced adsorption rate beyond 4 hours reflects surface site saturation and a diminished concentration gradient driving diffusion.[18]

Figure 2C illustrates the influence of initial MB concentration on adsorption capacity, which increases almost linearly from 37.23±0.03 mg/g at 5 mg/L to a maximum of 295.09±0.04 mg/g at 40 mg/L. This phenomenon is explained by the increased concentration gradient between the bulk solution and the interior of the adsorbent particles, which promotes deeper diffusion of MB molecules.[18] Additionally, osmotic swelling of the composite beads facilitates further penetration of MB within the adsorbent matrix.

Conversely, Figure 2D demonstrates that temperature exerts an inverse effect on adsorption capacity. As the temperature rises from 303 K to 333 K, the adsorption capacity decreases, indicating that the adsorption process is exothermic, consistent with prior reports. The reduction in adsorption capacity at elevated temperatures is attributed to weakened interactions between MB molecules and active adsorption sites, alongside enhanced solubility and desorption rates of MB dye.[18]

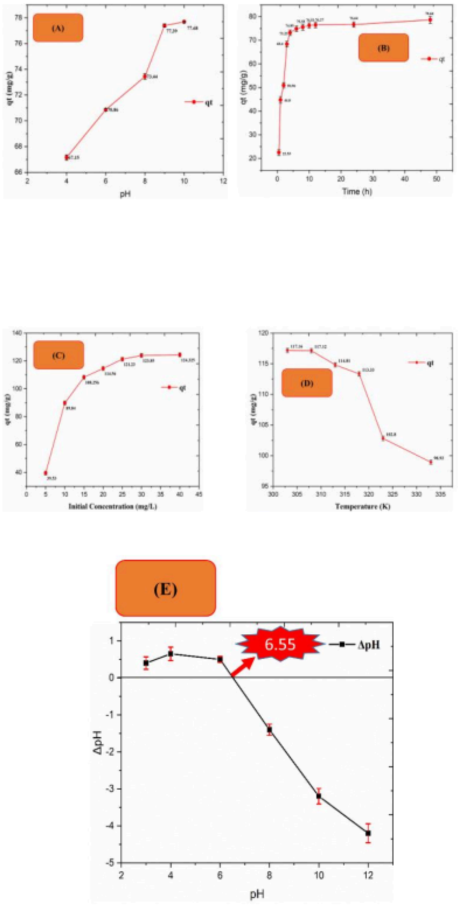


Figure 2. Effects of pH (A), time (B), initial concentration (C), temperature (D), and pH_{pzc} of the ACPU adsorbent (E).

3.3. Adsorption Kinetics

Kinetic modeling was employed to elucidate the adsorption mechanism of MB onto ACPU composite particles and to optimize the adsorption process. As illustrated in Figure 3, the experimental data closely followed the pseudo-second-order (PSO) kinetic model, as evidenced by the high correlation coefficient (R^2 approaching 1). The calculated equilibrium adsorption capacity ($q_e = 161.12 \pm 0.03$ mg/g) closely matched the experimentally observed value (150.32±0.03 mg/g), confirming the model's validity. These findings are consistent with those reported by Luong et al. (2024) for graphene oxide/chitosan granular adsorbents.[17]

Given the granular structure of the adsorbent, the intraparticle diffusion model was further applied to gain deeper insight into the adsorption kinetics (Figure 3A). In the initial stage, a steep slope ($k_{p1} = 0.312$ mg/g·min$^{0.5}$) was observed, indicating rapid external surface adsorption and diffusion across the boundary layer. The associated parameters $R_{i1} = 0.2437$ and $C/q_{ref} = 0.7805$ fall within region 3, which characterizes strong initial adsorption activity. In the subsequent stage, the slope decreased significantly ($k_{p2} = 0.0234$ mg/g·min$^{0.5}$), signifying slower diffusion into the internal pores of the adsorbent. The corresponding values $R_{i2} = 0.0297$ and $C/q_{ref} = 0.971$ are located in region 4, suggesting that over 90% of the total adsorption occurs during the initial phase.

Moreover, the fact that the two linear segments of the intraparticle diffusion plot do not intersect the origin indicates that the adsorption process is not governed solely by intraparticle diffusion. Instead, it likely involves multiple rate-limiting steps, including surface adsorption and possible chemical interactions between the adsorbate and active sites on the composite material.

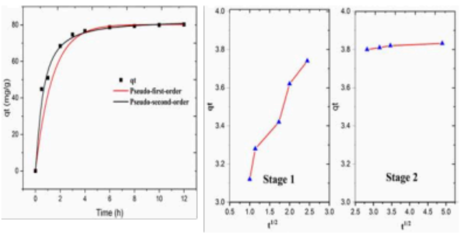


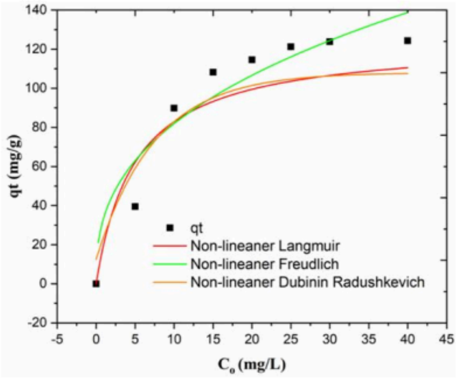
Figure 3. Pseudo-first-order model and Pseudo-second-order model (A), Intra-particle diffusion model (B) for MB adsorption by composite bead adsorbent ACPU.

3.4. Adsorption isotherms

Adsorption isotherms are vital tools for evaluating adsorption capacity, characterizing adsorbent–adsorbate interactions, and gaining insight into the surface properties of adsorbents. In this study, the experimental data were analyzed using two widely accepted isotherm models: Langmuir and Freundlich. The nonlinear Langmuir model at 303 K, as shown in Figure 4, yielded a maximum theoretical adsorption capacity of 951.35±0.03 mg/g with a correlation coefficient $R^2 = 0.974$ and a Langmuir constant $k_L = 0.298 \pm 0.02$. Although the relatively high R^2 value indicates a strong fit, it does not reach unity, implying that the experimental data deviate slightly from the assumptions of the Langmuir model, which states monolayer adsorption on a homogeneous surface.

Conversely, the nonlinear Freundlich model (Figure 4) provided an excellent fit to the data, with a correlation coefficient of $R^2 = 0.997$, suggesting that MB adsorption onto the ACPU composite beads is better described by this model. The Freundlich constant 1/n was calculated as 0.89, which is less than 1, indicating favorable adsorption. The relatively low slope of the fitted curve further supports this conclusion. These findings also suggest that the adsorption process is reversible and involves heterogeneous energy distributions across the adsorbent surface, allowing for multilayer adsorption.

To further explore the adsorption mechanism, the Dubinin–Radushkevich (D–R) isotherm model was applied to estimate the mean free energy and to assess the porosity characteristics of the adsorbent. The D–R model analysis yielded a mean free energy of 0.98±0.03 kJ/mol, which is significantly below the 8.0 kJ/mol threshold. This indicates that the adsorption process is predominantly governed by physical interactions.



In summary, the adsorption behavior of MB onto ACPU composite beads is best described by the Freundlich and Dubinin–Radushkevich models, suggesting multilayer, physical adsorption on a heterogeneous surface with variable adsorption energies.

Figure 4. Langmuir, Freundlich, Dubinin-Radushkevich non-linear isotherm for MB adsorption on composite bead adsorbent.

3.5. Thermodynamic Study

The effect of temperature on the adsorption of MB onto ACPU composite beads was evaluated through key thermodynamic parameters, including changes in enthalpy (ΔH°), entropy (ΔS°), and Gibbs free energy (ΔG°). The Gibbs free energy values were found to be negative at all studied temperatures, confirming that the adsorption process is spontaneous and thermodynamically favorable. Moreover, the negative enthalpy change ($\Delta H^o = -98.36 \pm 0.01$ kJ/mol) indicates that the adsorption is exothermic in nature, in agreement with previous observations.[18] The entropy change ($\Delta S^o = -0.12 \pm 0.04$ J/mol·K) was also negative, suggesting a decrease in disorder at the solid–liquid interface during adsorption. This reflects an increased ordering of MB molecules on the adsorbent surface, as they become more densely arranged upon interaction with the composite material.

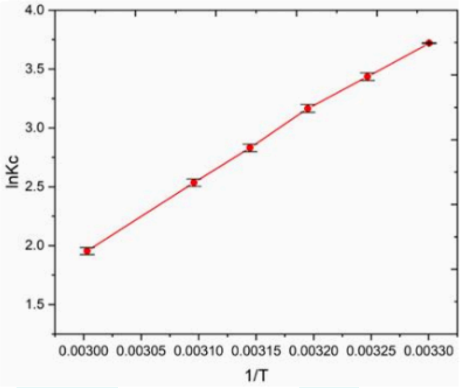


Figure 5. Van't Hoff plot for the adsorption of MB on ACPU composite bead.

4. CONCLUSION

In this study, a cost-effective and ecologically sustainable composite adsorbent was successfully developed using spent coffee grounds and biodegradable polymers. Structural analyses confirmed the formation of covalent Schiff base linkages and hydrogen bonding among components, yielding a mesoporous material with a surface morphology conducive to adsorption. The composite demonstrated strong adsorption affinity for MB, with kinetics following a PSO model and equilibrium behavior best described by the Freundlich and Dubinin–Radushkevich isotherms—indicating a multilayer, physical adsorption mechanism. Thermodynamic analysis revealed that the adsorption process was spontaneous and exothermic. Overall, the high adsorption capacity, combined with the renewable and low-cost nature of the raw materials, underscores the potential of this composite for practical application in wastewater treatment, particularly in the removal of cationic dyes from aqueous environments.

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