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. Các phương pháp phân tích đánh giá hiện đại xác nhận sự kết 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 ở pH 8, với dung lượng hấp phụ cực đại đạt 149,57 mg/g tại nồng độ MB 40 mg/L. Dữ liệu động học phù hợp với mô hình giả bậc hai, 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 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 with pore diameter 21.1 Å and 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 pH 8, with maximum uptake of 149.57 mg/g at 40 mg/L MB concentration. Kinetic data fitted the pseudo-second-order model, 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 highly 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.

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

Methylene blue dye (purity ≥ 99%) was purchased from Xilong Chemical Co., Ltd. (China). Chitosan, possessing a degree of deacetylation exceeding 80% and a molecular weight of 87 kDa, was obtained from S-Green Company (Vietnam). 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] Used coffee grounds were gathered, thoroughly washed with distilled water to eliminate surface impurities, and then dried at 60 °C. The dried material was carbonized in a muffle furnace at 850 °C for one hour. The resulting char was chemically activated by immersing it in 1 M phosphoric acid (H_3PO_4) at a solid:liquid ratio of 1:10 (w/v) for two hours at ambient temperature to increase its surface area and porosity. Following activation, the material was washed multiple times with distilled water using ultrasonic agitation until the rinse water reached a neutral pH. The activated carbon was then dried in an oven, ground into a fine powder, and sieved to ensure uniform particle size. This method effectively transforms agricultural waste into a valuable material suitable for use in environmental cleanup applications.

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] To synthesize the ACPU granular adsorbent, 4 g of activated carbon (AC) was dispersed in 100 mL of distilled water and subjected to ultrasonic treatment for 10 minutes at a frequency of 40 kHz and a power of 100 W to ensure uniform dispersion. Simultaneously, 4 g of chitosan was dissolved in 100 mL of 1% (v/v) acetic acid by continuous stirring at 65 °C for 2 hours, forming solution A. Solution B was prepared by dissolving 4 g of polyvinyl alcohol (PVA) in 100 mL of deionized water, followed by heating at 90 °C for 5 hours until complete dissolution. Solution C was made by dissolving 4 g of unsaturated polyester resin (UPE) in 100 mL of deionized water. The three solutions (A, B, and C) were then combined and stirred at 90 °C for 1 hour to obtain a homogeneous mixture. This mixture was added dropwise into a 0.25 M NaOH solution to form beads and left to solidify for 2 hours. The formed composite beads were then rinsed multiple times with distilled water until a neutral pH was reached. Crosslinking was carried out by immersing the beads in a 25% (v/v) glutaraldehyde solution with continuous stirring for 2 hours. Finally, the ACPU adsorbent beads were collected using a Whatman membrane filter, thoroughly washed with distilled water, and dried in a vacuum oven (Memmert VO101) at 60 °C under 0.6 bar pressure for 6 hours.

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, contact time, initial concentration, adsorbent dose, and temperature, employing a univariate experimental design. The concentration of MB in solution before and after reaching adsorption equilibrium was measured 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.

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

In this equation, C_0 (mg/L) represents the initial concentration of the solute, while C_e (mg/L) denotes its concentration at equilibrium. V (L) is the volume of the solution used, and m (g) refers to the amount of adsorbent applied during the adsorption process.

To evaluate the surface charge characteristics of the composite adsorbent under varying pH conditions, the point of zero charge (pH_pzc) was determined. In this method, 0.1 g of the adsorbent was mixed with 25 mL of a 0.1 M KCl solution in a 250 mL Erlenmeyer flask. The initial pH of the mixture was adjusted between 2 and 12 using either 0.1 M HCl or 0.1 M NaOH. The suspensions were then shaken and left to reach equilibrium over a 24hour period. After equilibration, the final pH of each sample was measured. The pH_pzc corresponds to the pH value at which there is no net change between the initial and final pH ($\Delta pH = 0$). This measurement is important for understanding how the adsorbent's surface charge varies with pH, which in turn influences its ability to interact with charged species in solution[10].

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 MB onto the composite adsorbent.[11]

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

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

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

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

In this formulation, k_1 (1/min) is the rate constant for the pseudo-first-order model, k_2 (g/mg·min) stands for the pseudo-second-order rate constant, and k_p (mg/g·$min^{1/2}$) characterizes the intra-particle diffusion rate.

Adsorption isotherms are key to understanding the equilibrium between MB and the ACPU composite. The Langmuir model assumes monolayer adsorption on a uniform surface, while the Freundlich model describes multilayer adsorption on heterogeneous sites. To further assess the adsorption type, the Dubinin–Radushkevich (D–R) model was used. It differentiates between physical and chemical adsorption based on the mean energy (E), where $E < 8.0$ kJ/mol indicates physisorption and $E > 8.0$ kJ/mol suggests chemisorption.[11]

Langmuir isotherms:

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

In this equation, q_e (mg/g) indicates the quantity of adsorbate adsorbed per gram of adsorbent at equilibrium, while C_e (mg/L) refers to the equilibrium concentration of the adsorbate in solution. The parameters q_{max} (mg/g) and K_L (L/mg) are Langmuir constants that represent the theoretical maximum adsorption capacity and the adsorption affinity, respectively.

Freundlich isotherms:

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

In this equation, K_F (mg/g) and 1/n are Freundlich characteristic constants representing adsorption capacity and adsorption intensity, respectively

Dubinin–Radushkevich (D–R) isotherms:

$$\ln q_e = \ln q_m - \beta.\varepsilon^2 \quad (8)$$

In this equation, β is a parameter associated with the mean adsorption energy per mole of adsorbate (mol^2/J^2), while ε represents the Polanyi potential, which is determined using the following equation.

Thermodynamic assessment, often performed through the Van't Hoff equation, yields crucial parameters including Gibbs free energy change (ΔG°), enthalpy change (ΔH°), and entropy change (ΔS°). These thermodynamic indicators help clarify the spontaneity, feasibility, and energy dynamics involved in the adsorption process.

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (9)$$

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

In this formulation, T (K) is the absolute temperature and R (8.314 J/mol·K) denotes the universal gas constant. The equilibrium constant

is represented by Kc. These thermodynamic values are typically derived from the linear plot of ln Kc against 1/T. Additionally, C_0 and C_e (mg/L) indicate the initial and equilibrium concentrations of methylene blue (MB), respectively.

2.4. Physicochemical properties of adsorbent

To examine the functional group transformations of the composite beads, Fourier-transform infrared (FT-IR) analysis was conducted with a NICOLET 6700 spectrophotometer (Thermo), operating within the wavelength range of 4000 to 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.

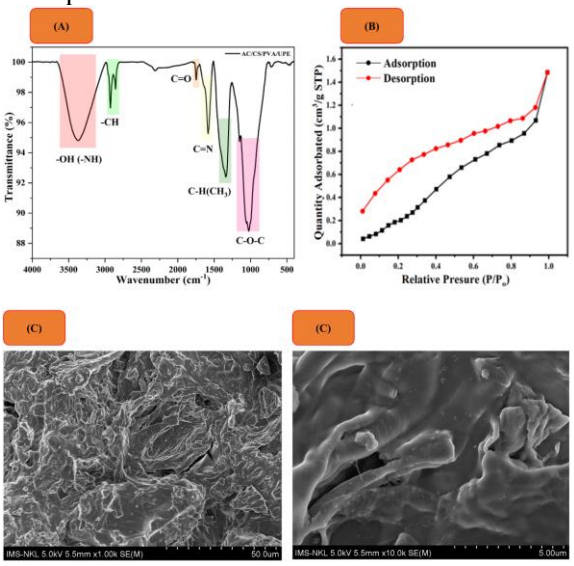

Figure1. Physicochemical properties of adsorbent FT-IR (A), adsorption/desorption N_2 (B), and x1,000 and x10,000 (C).

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. Specifically, as pH ranges from 6.0 to 10.0, the adsorption capacity escalates from 141.71±0.05 mg/g to 155.36±0.02 mg/g at pH 10.0. In the pH range above pH_{pzc}, the material's surface charge is primarily negative, enhancing the adsorption process. 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, the adsorption capacity increased significantly from 0.5 h (49.87±0.04 mg/g) to 4 h (143.26±0.02 mg/g). However, the adsorption capacity increased not much from 4 h (143.26±0.02 mg/g) to 48 h (153.73±0.03 mg/g). 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 h reflects surface site saturation and a diminished concentration gradient driving diffusion.[18]

Figure 2C illustrates the influence of initial MB concentration on adsorption capacity, Overall, as the initial MB concentration rose from 5 to 40 mg/L, the adsorption capacity demonstrated an essentially ascending trend from 17.14±0.03 mg/g to 157.87±0.04 mg/g. Even though more than 85% of MB was adsorbed at lower concentrations, this was due to an excess of active sites on the adsorbent's surface relative to the available adsorbate. On the other hand, the adsorption capacity increased to 157.87±0.04 mg/g as the MB concentration rose to 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.

On the other hand, Figure 2D indicates that increasing temperature negatively affects the adsorption capacity. As the temperature rises by 30 K from 303 K to 333 K, a noticeable decline in the amount of MB adsorbed occurs,

implying that the process is exothermic in nature an observation consistent with earlier studies. This reduction in adsorption performance at elevated temperatures is likely due to the diminished interaction strength between MB molecules and active sites, along with an increase in both dye solubility and desorption rate.[18]

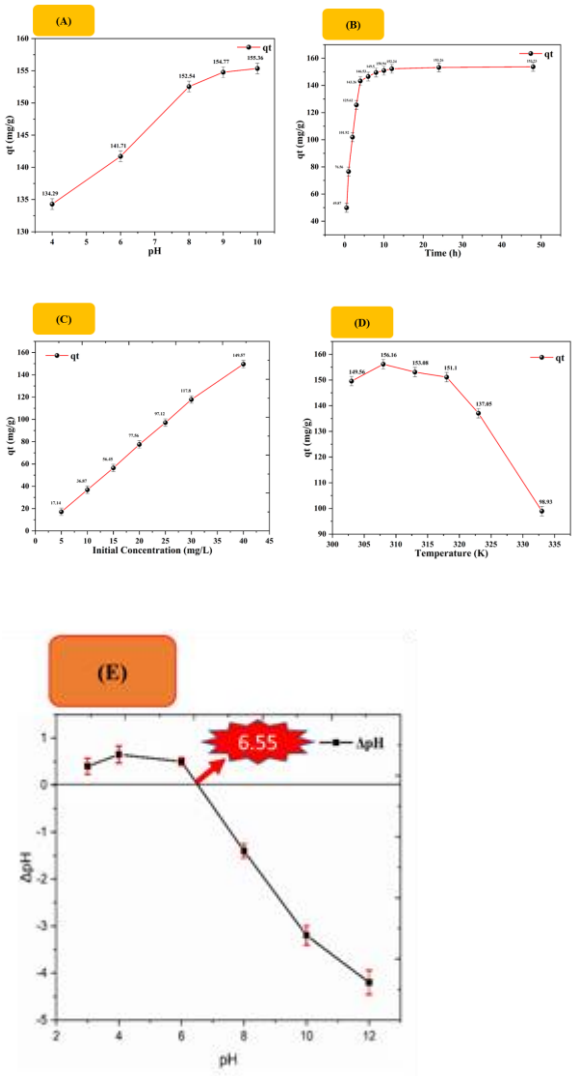

Figure 2. Influence of pH (A), contact time (B), initial dye concentration (C), temperature (D), and point of zero charge (pH_{pzc}) of adsorbent (E).

3.3. Kinetic Analysis of MB Adsorption

Kinetic modeling was applied to better understand the adsorption behavior of MB on ACPU composite beads and to support the optimization of the process. As shown in Figure 3, the experimental results aligned well with the pseudo-second-order (PSO) model, as indicated by a correlation coefficient (R^2) very close to unity. 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. The results obtained align with those documented by Luong et al. (2024), who reported similar adsorption behavior for granular adsorbents composed of graphene oxide and chitosan.[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.

Additionally, the fact that the two linear regions of the intraparticle diffusion curve fail to intersect the origin indicates that intraparticle diffusion is not the sole mechanism controlling the adsorption process. This suggests the involvement of multiple rate-limiting stages, including surface adsorption and possible chemical interactions between the adsorbate and the functional sites of the composite adsorbent.

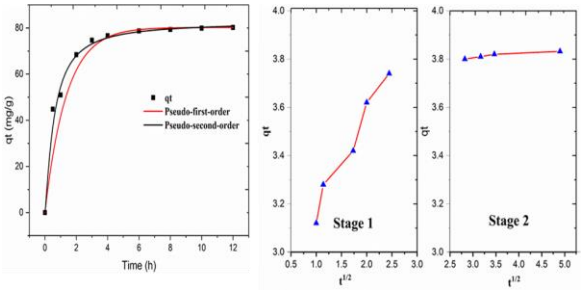

Figure 3. (A) Kinetic fitting using pseudo-first-order and pseudo-second-order models, and (B) intra-particle diffusion analysis for the adsorption of methylene blue (MB) onto adsorbent beads.

3.4. Isotherms of Adsorption Behavior

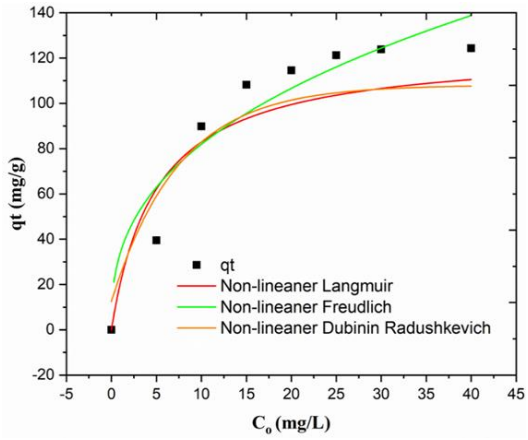

Figure 4. The adsorption of MB onto the composite beads was analyzed using non-linear forms of the Langmuir, Freundlich, and Dubinin–Radushkevich isotherm models.

Adsorption isotherms are used to evaluate adsorption capacity and surface properties. This study applied Langmuir and Freundlich models to analyze the data. At 303 K, the nonlinear Langmuir model predicted a maximum adsorption capacity of 841.64±0.02 mg/g, with an R^2 of 0.974 and a Langmuir constant of 0.298±0.02. Although the high R^2 indicates a good fit, it is slightly less than 1, suggesting minor deviations from the ideal monolayer adsorption assumption. Conversely, the nonlinear Freundlich model (Figure 4) 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. The D–R isotherm model was employed to examine the adsorption mechanism and pore structure. A mean free energy of 0.98±0.03 kJ/mol, far below 8.0 kJ/mol, suggests that physical adsorption is the dominant process.

3.5. Thermodynamic Study

The effect of temperature on MB adsorption by ACPU composite beads was analyzed through thermodynamic parameters. The negative values of ΔG^o across all temperatures indicate that the adsorption occurs spontaneously and is thermodynamically favorable. A negative enthalpy change ($\Delta H^o = -98.36 \pm 0.01$ kJ/mol) confirms the exothermic nature of the process, aligning with previous results. Furthermore, the negative entropy change ($\Delta S^o = -0.12 \pm 0.04$ J/mol·K) suggests decreased randomness at the solid–liquid interface, implying a more structured arrangement of MB molecules on the bead surface.

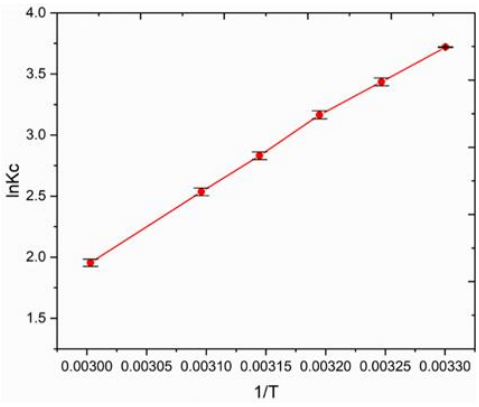

Figure 5. Thermodynamic analysis of MB adsorption onto ACPU beads based on the Van't Hoff equation.

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 D–R 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 solution.

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