Chất Hấp Phụ Dạng Hạt Thân Thiện Môi Trường Từ Than Hoạt Tính Nguồn Gốc Bã Cà Phê Ứng Dụng Xử Lý Nước Thải

TÓM TẮT

Nghiên cứu này tạo ra chất hấp phụ dạng hạt thân thiện môi trường có nguồn gốc từ bã cà phê dùng cho xử lý nước thải. Than hoạt tính (AC) được tổng hợp từ bã cà phê và kết hợp với chitosan (CS) và alginate (AL) để tạo thành vật liệu composite, CAA, nhằm tăng cường khả năng loại bỏ thuốc nhuộm. Quá trình tổng hợp được tối ưu hóa bằng cách điều chỉnh các tham số chính, bao gồm khối lượng AC, nồng độ NaOH và thời gian ngâm, để tối ưu hóa hiệu quả hấp phụ. Hiệu năng của vật liệu được đánh giá bằng cách sử dụng thuốc nhuộm Malachite xanh (MG) làm chất ô nhiễm mô hình. Các đặc trưng cấu trúc và hóa học, bao gồm phân tích nhiệt trọng lượng (TGA) và quang phổ hồng ngoại biến đổi Fourier (FT-IR), xác nhận sự tổng hợp thành công của chất hấp phụ composite. Kính hiển vi điện tử quét (SEM) cho thấy phân bố kích thước hạt đồng đều, bề mặt thô và cấu trúc xốp phát triển tốt. Với diện tích bề mặt riêng là 11,231 m^2/g và cấu trúc mao quản có đường kính lỗ 12,887 Å, chất hấp phụ này cho thấy tiềm năng mạnh mẽ trong xử lý nước thải. Những phát hiện này củng cố việc sử dụng than hoạt tính từ bã cà phê như một giải pháp bền vững và tiết kiệm chi phí để loại bỏ các chất ô nhiễm hữu cơ, đặc biệt là thuốc nhuộm, từ nước thải.

Từ khoá: *Than hoạt tính, Hấp phụ, Chất hấp phụ dạng hạt, Malachite xanh, Bã cà phê.*

Eco-Friendly Granular Adsorbent Based Activated Carbon from Spent Coffee Grounds for Wastewater Treatment

ABSTRACT

This study discovers the development of an eco-friendly granular adsorbent derived from spent coffee grounds for wastewater treatment. Activated carbon (AC) was synthesized from spent coffee grounds and combined with chitosan (CS) and sodium alginate (AL) to form a composite material, CAA, for enhanced dye removal. The synthesis process was optimized by adjusting key parameters, including AC mass, NaOH concentration, and soaking time, to maximize adsorption efficiency. The effectiveness of the material was evaluated using Malachite Green (MG) dye as a model pollutant. Comprehensive structural and chemical characterizations, including thermogravimetric analysis (TGA) and Fourier transform infrared spectroscopy (FT-IR), confirmed the successful formation of the composite adsorbent. Scanning electron microscopy (SEM) revealed a uniform particle size distribution, rough surface morphology, and well-developed porous structure. With a specific surface area of 11.231 m²/g and a mesoporous structure featuring a pore diameter of 12.887 Å, the adsorbent demonstrates strong potential for wastewater treatment. These findings highlight the promising use of coffee-ground-derived activated carbon as a sustainable and cost-effective solution for the removal of organic pollutants, specifically dyes, from wastewater.

Keywords: *Activated Carbon, Adsorption, Granular Adsorbent, Malachite Green, Spend Coffee Grounds.*

1. INTRODUCTION

As sustainability, resource efficiency, and economic viability continue to gain prominence, agricultural by-products are increasingly being utilized across various industries, offering innovative solutions to waste management challenges while promoting environmentally friendly alternatives to conventional materials.[1] The growing focus on circular economy principles highlights the vital role of agricultural wastes in advancing environmental sustainability. Among these agricultural by-products, spent coffee grounds have emerged as a promising raw material for the production of activated carbon (AC), a highly effective adsorbent for environmental remediation, particularly in wastewater treatment.[2]

Water pollution caused by synthetic dyes from industries such as textiles, leather, and paper manufacturing remains one of the most pressing environmental concerns. These dyes, often toxic, persistent, and non-biodegradable, pose a significant threat to aquatic ecosystems by blocking light penetration, disrupting photosynthesis, and depleting oxygen levels in water.[3] Furthermore, many synthetic dyes contain carcinogenic and mutagenic compounds that can bioaccumulate in aquatic organisms, causing long-term ecological and health risks. Traditional methods, including photocatalysis, biodegradation, membrane filtration, electrochemical oxidation, and coagulation, have been developed to address this issue, but each method comes with its own set of limitations, such as high energy demands, chemical usage, and slow processing times.[4]

Among these treatment methods, adsorption using activated carbon has proven to be one of the most effective, offering advantages like simplicity, high efficiency, low energy consumption, and the ability to remove a wide range of organic pollutants, including dyes.[5] However, the use of powdered or fine-grained activated carbon (AC) presents challenges in terms of recovery, reusability, and mechanical stability, limiting its widespread application in large-scale wastewater treatment.[6]

In response to these challenges, this study introduces an innovative solution by developing eco-friendly granular adsorbents derived from spent coffee grounds. By integrating activated carbon with biopolymers such as chitosan (CS) and sodium alginate (AL), this study enhances the adsorbent's structural stability and efficiency in dye removal. Chitosan, a biodegradable and non-toxic biopolymer, and sodium alginate, known for its gel-forming capabilities and high water stability, offer valuable functional groups that further improve the adsorptive properties of the material.[7] This approach not only provides a sustainable method for coffee ground waste utilization but also contributes to an effective, environmentally friendly solution for wastewater treatment and the removal of organic pollutants.

2. Material and Methods

2.1. Material

In this study, spent coffee grounds were collected from Trung Nguyen coffee shops in Can Tho City, providing an abundant, sustainable raw material for the production of activated carbon. The chemicals used in the synthesis process included phosphoric acid, sodium hydroxide, sulfuric acid, acetic acid, and potassium chloride, all sourced from Xilong Scientific Co., Ltd., which played a crucial role in optimizing the activation and composite formation. Chitosan powder, a biodegradable and eco-friendly biopolymer, was supplied by S-Green Co., Jsc, while sodium alginate, known for its gel-forming properties and water stability, was obtained from Shanghai Zhanyun. Together, these materials were combined to create a granular composite adsorbent that integrates the sustainability of spent coffee grounds with the enhancing properties of natural biopolymers, paving the way for an efficient, eco-friendly solution to wastewater treatment.

2.2. Preparation of activated carbon from coffee grounds

The spent coffee grounds were carefully collected, washed with distilled water to remove surface impurities, and then dried at 50 °C to prepare them for further processing. After drying, the moisture content and mass of the coffee grounds were accurately measured using a moisture analyzer to ensure consistency. The dried grounds were then subjected to carbonization at 850 °C for 1 h in an oven, transforming them into raw activated carbon. To enhance the adsorptive properties, the resulting carbon was activated by soaking in a 1 M phosphoric acid (H_3PO_4) solution at a ratio of 1:10 (w/v) for 2 h at room temperature. This activation process allowed the formation of a highly porous structure, ideal for pollutant adsorption. After activation, the carbon was meticulously washed with distilled water through ultrasonic waves to remove any residual chemicals, continuing until a neutral pH was achieved. Finally, the activated carbon (AC) was dried, ground, and sieved to obtain fine particles with a diameter of less than 80 μm, ensuring its suitability for effective wastewater treatment and adsorption applications. This process not only transforms spent coffee grounds into a valuable resource but also highlights the potential of sustainable materials for environmental remediation.

2.3. Synthesis of composite bead adsorbent on activated carbon base derived from coffee grounds

In this study, an eco-friendly granular composite adsorbent was developed by combining activated carbon (AC) derived from spent coffee grounds with biopolymers, chitosan (CS) and sodium alginate (AL), through a gel-ion self-association method. To begin, a CS solution was prepared by dissolving 1 gram of chitosan in 25 mL of 2% (v/v) acetic acid, creating a smooth gel. AC was then added to the chitosan solution at a specified mass ratio and stirred until a uniform dispersion was achieved. To form the granular composite adsorbent, the CS-AC suspension was carefully dispensed through a syringe into a sodium hydroxide (NaOH) solution, where the chitosan was rapidly condensed, shaping the material into granular particles within a set time. The adsorbent particles were then filtered, washed with distilled water, and adjusted to a near-neutral pH.

Next, the CS-AC adsorbent was functionalized by soaking it in a 2% (w/v) sodium alginate (AL) solution for 2 hours then continue to soak in 2.5% (w/v) $CaCl_2$ solution for 2 hours at room temperature, shaking at 100 rpm, allowing the AL to bind with the material, further enhancing its adsorptive properties. After filtration and washing to neutral pH, the composite adsorbent was dried under vacuum conditions (600 mbar, 60 °C) for 5 h to obtain the final granular adsorbent material—CAA—

designed for the effective adsorption of organic dyes from aqueous solutions.

The synthesis process of the CAA composite adsorbent was optimized by investigating the adsorption of Malachite Green (MG) dye under controlled conditions: an initial concentration of 20 ppm, adsorbent mass of 0.2 g, dye solution volume of 25 mL, contact time of 24 h, and shaking speed of 150 rpm. The dye concentration at equilibrium was measured using UV-Vis molecular absorption spectroscopy at the maximum absorption wavelength of 617 nm. The adsorption capacity (q_t, mg/g) and the removal efficiency (%) of MG were calculated to evaluate the effectiveness of the adsorbent via equation (1) and (2), demonstrating the potential of this eco-friendly composite material as a sustainable solution for wastewater treatment and organic dye removal.

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

$$H = \left(\frac{C_o - C_e}{C_o}\right).100 \qquad (2)$$

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.

2.4. The characteristic properties of synthetic granular adsorbent materials

To fully understand the properties and performance of the developed eco-friendly granular composite adsorbent (CAA), a comprehensive set of characterization techniques was employed. The surface morphology of the composite material was analyzed using the Scanning Electron Microscope (SEM) by Horiba. This provided detailed insights into the structural features, including particle size distribution, surface roughness, and pore development, essential for understanding the material's potential in pollutant adsorption. Thermogravimetric analysis (TGA) was conducted to evaluate the thermal stability and mass changes of the adsorbent during processes such as decomposition, oxidation, and reduction. The analysis was carried out in a nitrogen atmosphere using the TGA-DSC3+ system (Mettler Toledo), with temperatures ranging from 25 °C to 1000 °C and a heating rate of 5 °C/min, providing valuable information on the material's thermal behavior.

The specific surface area and porosity of the composite adsorbent were measured using the Brunauer-Emmett-Teller (BET) method, based on nitrogen adsorption-desorption isotherms, with the 201A apparatus from Porous Materials-America. These measurements are critical for understanding the material's capacity to adsorb pollutants, as a higher surface area and well-developed pores enhance its efficiency. Lastly, the point of zero charge (pH_{pzc}) of the composite adsorbent was determined to understand its surface charge behavior in different pH environments. A 0.2 g sample of the AC-CS material was immersed in 25 mL of 0.1 M KCl solution in a 250 mL Erlenmeyer flask, and the pH was adjusted from 2 to 12 using 0.1 M NaOH and 0.1 M HCl. After 24 h, the final pH was recorded, and the pH_{pzc} value was determined graphically, providing further insights into the material's interaction with pollutants in wastewater.

Through these characterizations, this work was able to comprehensively evaluate the eco-friendly granular composite adsorbent's structural, thermal, and chemical properties, confirming its potential as an effective and sustainable solution for wastewater treatment and organic dye removal.

3. RESULT AND DISCUSSION

3.1. Parameters influencing the synthesis of granular adsorbent CAA.

3.1.1. Influence of activated carbon (AC) content

The effect of activated carbon (AC) content on the fabrication and performance of the eco-friendly granular composite adsorbent is highlighted in Figure 1. The experimental results reveal that the AC content plays a crucial role in both the adsorption capacity and structural integrity of the composite material, directly influencing its effectiveness in removing Malachite Green (MG) dye from aqueous solutions.

As the AC mass increased from 1 g to 5 g, the adsorption efficiency of the composite material significantly improved, with removal efficiencies of 63.40±3.51%, 66.25±2.37%, 77.65±3.45%, 78.55±4.89%, and 80.15±2.88%, respectively (Figure 1B). This trend demonstrates a clear correlation between the AC content and the material's ability to remove MG dye, suggesting that a higher concentration of AC enhances the adsorption capacity. The functional groups of AC, particularly –OH and –COOH groups, are key contributors to this improved performance.[8] The –OH groups facilitate the swelling of the material through hydrogen bonding with the nitrogen and oxygen atoms in MG molecules, while the –COOH groups ionize to form –COO$^-$, which further strengthens ionic interactions, attracting the oppositely charged regions of the dye molecules.[8]

However, the AC content also significantly impacts the granulation process of the composite adsorbent. As shown in Figure 1A, when the AC content was below 3 g, the resulting droplets failed to form stable, well-structured granules. These fragile formations lacked the mechanical strength required to withstand external forces during the granulation process, leading to structurally weak adsorbents that were unsuitable for practical applications. Hence, achieving an optimal balance of AC content is essential to ensure both high adsorption efficiency and robust structural stability.

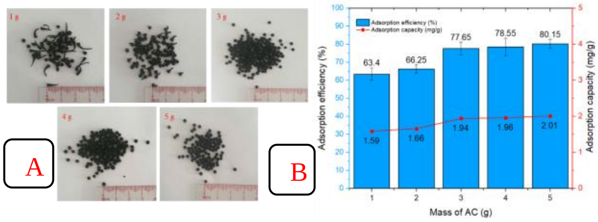

Figure 1. Influence of activated carbon (AC) content on the formation of adsorbent (A) and the removal ability of Malachite Green (B).

3.1.2. Influence of NaOH

In this study, NaOH solution was employed as the solvent for preparing the eco-friendly CAA granular adsorbents, utilizing a phase inversion process to achieve stable granule formation. The phase inversion technique involves transforming CS from its gel phase back into a solid state through the modification of its glycosidic bonds.[9] This process occurs in two critical stages: gelation, where a gel structure is formed, and precipitation, where the structure solidifies. The precipitation is driven by an acid-base reaction, which begins when CS is dissolved in a 2% (v/v) acetic acid solution. In this acidic medium, the amine groups (-NH_2) on the CS molecules accept protons, forming positively charged ammonium groups (-NH_3^+). This protonation increases chitosan's polarity and solubility in water, allowing it to remain in solution.

The precipitation process is initiated when the CS-AC mixture is introduced into the NaOH solution. At the interface between the liquid droplets and the NaOH solution, the hydroxide ions (OH^-) neutralize the ammonium groups (-NH_3^+), reducing the polarity of the CS.[10] This rapid neutralization triggers chitosan's precipitation, initially forming a gel layer on the particle surface. Over time, the excess hydroxide ions further facilitate the transition from the gel phase to a solid precipitate, ultimately resulting in mechanically stable, granular adsorbents. [10]

The impact of NaOH concentration on the synthesis of CAA granules is depicted in Figure 2A. As the NaOH concentration increased, the stability of the precipitation process improved, resulting in more uniform-sized particles with a stable surface. This enhanced stability was observed to be beneficial for creating well-formed granules, ideal for practical applications. However, an excessively high NaOH concentration posed a challenge: it could completely neutralize the cations on the particle surface, disrupting electrostatic interactions. This disruption hindered the subsequent immersion in the sodium alginate solution, negatively affecting the material's adsorption capacity.[11]

Figure 2B at a NaOH concentration of 1.25 M, the granule formation process is rapid, but the adsorption efficiency is limited, reaching only 62.55±4.51%. As the NaOH concentration decreases, the MG adsorption efficiency increases. At NaOH concentrations of 0.25 M, 0.5 M, and 0.75 M, the adsorption results were similar; however, granules formed at 0.75 M NaOH exhibited more uniformity and durability compared to those formed at 0.25 M and 0.5 M concentrations. Therefore, a NaOH concentration of 0.75 M was selected for synthesising the granules for subsequent investigations.

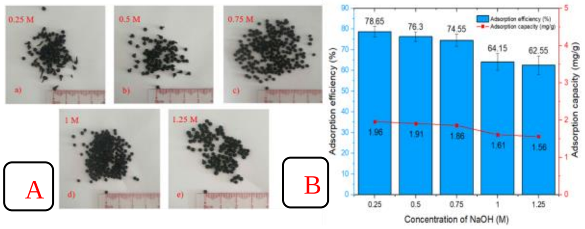

Figure 2. Influence of NaOH concentration on the formation of adsorbent (A) and the removal ability of Malachite Green (B).

3.1.3. Influence of soaking time in NaOH

Figure 3 demonstrates the effect of soaking time in a 0.75 M NaOH solution on the adsorption efficiency of MG dye by the eco-friendly granular adsorbent. As the soaking time increased from 30 to 150 min, a noticeable decrease in MG adsorption efficiency was observed. The adsorbent soaked for 30 min exhibited the highest adsorption efficiency at 83.10±0.73%, but the granules were poorly shaped and fragile, making them prone to mechanical breakage. This highlights the challenge of balancing effective adsorption with the mechanical stability of the granules.

Based on the adsorption data, the optimal soaking time was found to be 60 min, where a balanced combination of high adsorption efficiency (77.20±1.05%) and well-formed granules was achieved. The granules produced at this soaking time exhibited good structural integrity, making them suitable for practical applications while maintaining relatively high dye removal performance. As the soaking time was extended beyond 60 min, the adsorption efficiency gradually decreased. Specifically, at 90 min, the efficiency dropped to 74.15±1.35%, and by 150 min, it reached 68.85±1.72%. This decline in adsorption performance can likely be attributed to the over-modification of the material's structure or degradation of adsorption sites as a result of prolonged exposure to the NaOH solution.[12] Prolonged soaking could also lead to a loss of functional groups essential for dye removal due to chitosan is susceptible to glycosidic bond cleavage and denaturation of amino groups –NH_2, leading to a decrease in the number of adsorption sites, further diminishing the material's efficiency[13].

These findings emphasize that while NaOH treatment is crucial for enhancing the adsorption capacity of the adsorbent, excessive soaking can have detrimental effects. Therefore, a soaking time of 60 min is considered optimal, providing the ideal balance between adsorption performance and structural stability. This soaking time was selected as the standard condition for all subsequent experiments, ensuring the production of an efficient and durable adsorbent material for wastewater treatment applications.

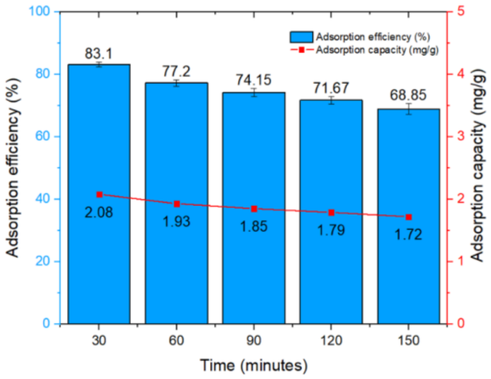

Figure 3. Influence of soaking time in NaOH on the removal ability of Malachite Green.

3.2. The characteristic properties of synthetic granular adsorbent materials

3.2.1. Surface morphology of CAA granular adsorbent

The surface morphology and internal structure of the eco-friendly CAA adsorbent particles were thoroughly examined using scanning electron microscopy (SEM). The images presented in Figure 4A and 4B, captured at different resolutions, reveal the highly porous internal structure of the adsorbent. The material, composed of AC integrated with CS and AL, demonstrates well-developed capillary pores ranging from 13 to 18 µm in size (Figure 4E). These uniform pores suggest that the adsorbent has an excellent capacity to adsorb and store molecules, which is crucial for its effectiveness in dye removal during wastewater treatment.

Further examination of the surface morphology in Figure 4C and 4D shows a distinctive combination of concave and convex surface features. The surface is characterized by grooves, cracks, and blocks of varying sizes, which not only contribute to the material’s mechanical stability but also increase the surface area available for adsorption. These structural features, along with the porous capillary system, provide additional surface roughness and fractures, creating multiple potential adsorption sites for contaminants.[13] This unique surface architecture is expected to enhance the adsorbent's overall capacity to capture and retain organic pollutants, such as MG dye, from aqueous solutions.

Additionally, the white areas observed on the particle surface are likely a result of the AL component, formed after the cross-linking process. This suggests that the AL polymer plays a key role in the structural integrity and functionality of the adsorbent, likely contributing to its stability and enhancing its ability to interact with pollutants.

The SEM analysis highlights the exceptional design of the CAA adsorbent, which combines a porous internal structure with a rough and varied surface morphology. This makes the material highly effective for wastewater treatment applications, capable of adsorbing a wide range of contaminants while maintaining the necessary physical strength and stability for practical use.

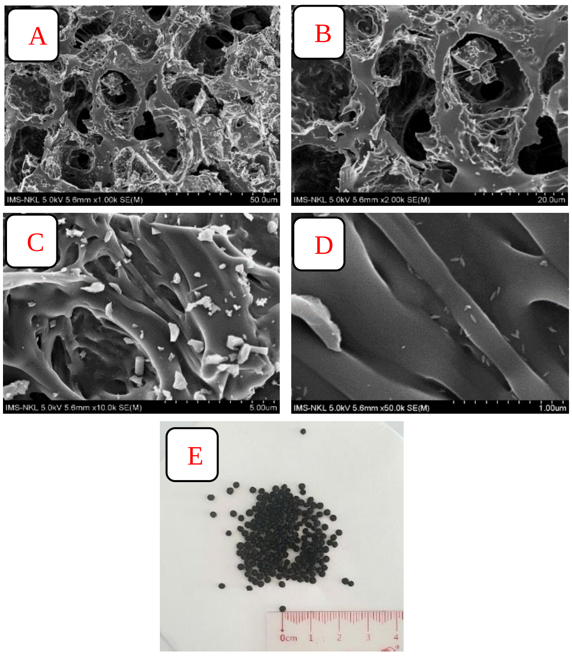

Figure 4. Internal morphology of granular adsorbent material at different magnifications X1,000 (A), X2,000 (B); External surface morphology of the material at different magnifications X10,000 (C), X50,000 (D); Digital image of granular adsorbent material (E).

3.2.2. Thermogravimetric analysis (TGA)

The thermal stability of the granular adsorbent, was assessed through thermogravimetric analysis (TGA) and differential thermogravimetric (DTG) curves, as shown in Figure 5A. The thermal decomposition behavior of the AC, produced by a mechanical method, activated at 850 °C, and further treated with H_3PO_4, reveals three distinct stages of mass loss, each indicative of different material properties.

The first stage, occurring between 29 °C and 100 °C, is associated with the evaporation of both physical and chemically bound water and the decomposition of volatile organic materials. This phase results in a relatively small mass loss of 5.2%.[14] The peak observed at 82.76 °C in the differential scanning calorimetry (DSC) curve confirms the exothermic nature of water evaporation, highlighting the removal of moisture from the carbonized material.

The second stage, between approximately 200 °C and 410 °C, is marked by the decomposition of hemicellulose, followed by the breakdown of cellulose at around 455 °C, accompanied by the degradation of the carbon skeleton.[15] This stage represents the most significant mass loss of 56.6%, highlighting the breakdown of the organic components in the material. The peak at 284.54 °C in the DSC curve emphasizes the endothermic nature of this decomposition process. As the material undergoes pyrolysis, the carbon structure begins to form, and volatile organic components are released.

The third stage, occurring between 500 °C and 600 °C, reflects the decomposition of the amorphous cellulose regions, oxidation of the cellulose carbon skeleton, and breakdown of lignin in the sample.[15] This stage produces carbon gases such as CO and CO_2, as the high molecular weight compounds dissociate into lower molecular weight fragments. The DSC peak at 812.13 °C further corroborates the breakdown of hemicellulose and cellulose during pyrolysis, with the slow degradation of lignin evident in the extended tail of the DTG curve. This suggests passive pyrolysis beyond 550 °C, where slight volatilization occurs as C–C and C–H bonds are cleaved, contributing to the thermal carbonization of the biomass.[14]

The thermal analysis of the composite granular adsorbent (CAA) is presented in Figure 5B, where the first stage, occurring between 25 °C and 185 °C, corresponds to initial mass loss due to both physical and chemical dehydration. During this phase, the vitrification transition of CS leads to a significant mass reduction of 12.86%, as indicated by the DSC peak at 121.5 °C, which confirms the exothermic phase change of the CS.

In the subsequent stages, CS and AL are progressively decomposed. This stage, occurring between 200 °C and 400 °C, results in the breakdown of AL and the formation of $CaCO_3$, which is typical of the cross-linking process involving sodium alginate. The combined thermal behavior of all CS, AL, and AC is reflected in the DTG curve, showing the distinct contributions of each component to the thermal stability and structural integrity of the CAA.

These findings underscore the complex thermal behavior of the CAA adsorbent, revealing the critical role of each component in determining the material's stability. The combination of AC derived from spent coffee grounds with biodegradable biopolymers like CS and AL results in a highly stable, environmentally friendly adsorbent, ideal for wastewater treatment applications. The thermal analysis further supports the feasibility of this material for practical use, demonstrating its robust structure and thermal resilience even under harsh conditions.

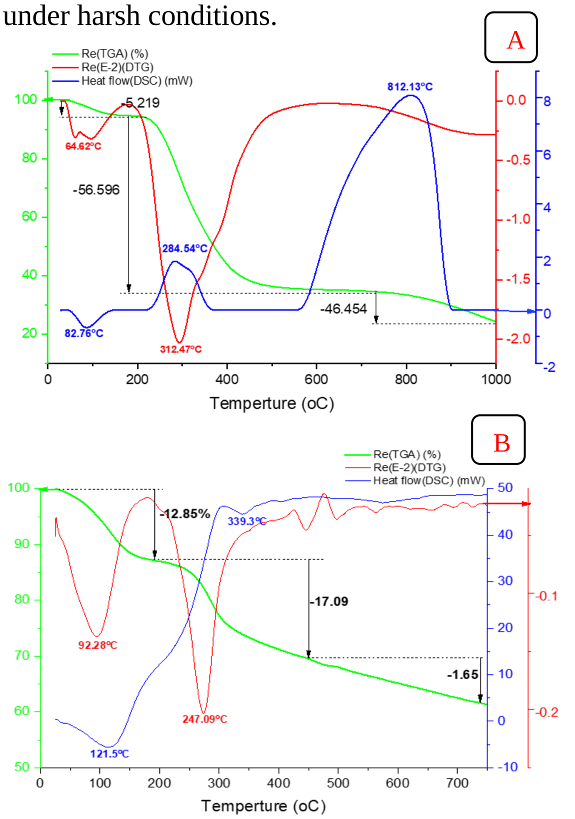

Figure 5. TGA/DTG and DSC diagrams of AC derived from coffee grounds (A) and CAA granular adsorbent (B).

3.2.3. Fourier Transform-infrared (FT-IR) spectroscopy

Fourier transform infrared (FT-IR) spectroscopy was employed to analyze the functional groups and chemical changes in the material before and after treatment. The FT-IR spectrum of AL exhibited characteristic peaks at 1333 cm^{-1} and 1032 cm^{-1}, corresponding to the C-H stretching vibration of glucose and the C-O stretching vibration of ether and alcohol groups, respectively, 2824 cm^{-1} represents the aliphatic C–H stretching vibration ($–CH_2–$, –CH–) characteristic of the polyuronic backbone of alginate, 2482 cm^{-1} the presence of this peak indicates that the alginate has been acidified. which are typical of alginate's chemical structure.[16] These functional groups play an essential role in the adsorption process by providing active sites for interactions with pollutants.

The FT-IR spectrum of CS, a key component in the composite adsorbent, displayed a prominent peak at 3577 cm^{-1}, corresponding to the N-H stretching vibration of the amino group, and another peak at 1635.3 cm^{-1} related to the N-H bending vibration of the primary amide group within the CS.[17] These functional groups are crucial for the adsorption of pollutants, such as MG, through electrostatic and hydrogen bonding interactions.

The AC spectrum displayed peaks at 1635 cm^{-1} and 1385 cm^{-1}, which are indicative of C=O bonds found in carboxyl and aromatic groups on the AC surface. These peaks suggest that the carbonization process introduces oxygen-containing functional groups, which are key to enhancing the adsorbent's ability to interact with organic pollutants in wastewater.

When comparing the FT-IR spectra of the CAA granular adsorbent, common functional groups such as O-H at 3420 cm^{-1}, 3449 cm^{-1}, and 3452 cm^{-1}, along with –COO, C=O, and C-O at 1647 cm^{-1}, 1541 cm^{-1}, and 1601 cm^{-1}, were observed in all materials.[18] These peaks are indicative of the successful incorporation of various components, including CS, AL, and AC, into the final composite material. The presence of these functional groups demonstrates the material's potential to interact with pollutants, particularly organic dyes like MG.

A small peak at 534 cm^{-1} attributed to the vibration of the Ca–O bond, confirming the formation of the gel network through ionic bonding between Ca^{2+} and the carboxylate group of alginate.[19] Moreover, the C-H bond at 1457 cm^{-1} suggests the formation of hydrogen bonds between the functional groups, particularly between CS and AC, which further enhances the material's stability and adsorption capacity.[20]

Since MG is a positively charged ion in aqueous solutions, it interacts electrostatically with the negatively charged functional groups on the adsorbent, particularly –COO and O-H.[21] These functional groups act as adsorption sites, facilitating the effective removal of MG from wastewater. The FT-IR analysis confirms the key role of the functional groups in enhancing the material's adsorption efficiency, which is critical for wastewater treatment applications.

Briefly, the FT-IR spectra of the CAA granular adsorbent demonstrate the successful incorporation of CS, AL, and AC from spent coffee grounds, which contribute to the material's ability to effectively adsorb organic dyes like MG. The presence of multiple functional groups, including hydroxyl, carboxyl, and amino groups, underscores the material's potential as an eco-friendly and efficient adsorbent for wastewater treatment.

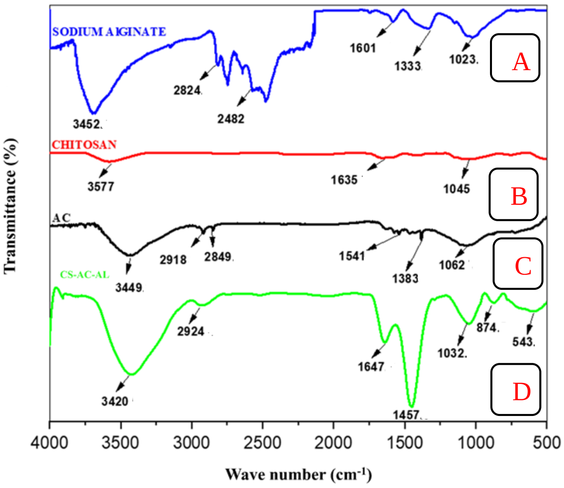

Figure 6. Fourier Transform-infrared (FT-IR) spectroscopy result of AL (A), CS (B), AC (C), The CAA granular adsorbent (D).

3.2.4. Adsorption/desorption N_2 isotherm (BET equation)

The specific surface area of the CAA granular adsorbent, derived from spent coffee grounds and AC using the BET (Brunauer-Emmett-Teller), BJH (Barrett–Joyner–Halenda) method, was analyzed to assess its potential for wastewater treatment applications. Nitrogen adsorption-desorption isotherms were used to evaluate the material's pore characteristics and adsorption capacity. The BET analysis revealed that the AC derived from spent coffee grounds exhibited a significantly higher adsorption compared to desorption, as shown in Figure 7. The surface area of the activated material was measured at 300.842 m²/g, indicating that the material possesses a relatively large surface area. This value is notably higher than many other adsorbents reported in previous studies, suggesting the material's superior adsorption potential.

The pore diameter of the AC was found to be 10.628 Å, placing the material within the micropore category. This observation aligns with the SEM analysis, which showed the presence of a highly porous structure. The high surface area and micropore distribution are crucial for efficient adsorption, as they provide numerous sites for pollutant molecules to interact with the adsorbent. These findings highlight that the material's high adsorption capacity reinforced by the IUPAC-type I adsorption isotherms is largely attributed to the large surface area created during the activation process.[20]

In contrast, the CAA granular adsorbent, prepared by incorporating CS and AL, showed a decrease in specific surface area to 11.231 m²/g compared to the raw AC. However, the pore diameter increased to 12.887 Å. This shift in pore characteristics is likely due to the formation of a granular structure during the condensation of CS, which encapsulated the AC. While the surface area decreased, the enlarged pores still ensured effective adsorption, indicating that the granular structure maintained sufficient adsorption sites for molecules.

Despite the increased pore size, the granular adsorbent still demonstrated significant adsorption potential. The 12.887 Å pore diameter is slightly larger than the size of MG dye molecules, which range from 0.8 to 1.58 nm. This suggests that the material can still effectively adsorb MG molecules, although the larger pore size might slightly hinder the diffusion of the dye into the adsorbent's structure. However, this slower diffusion is balanced by the material's long-term adsorption efficiency, as evidenced by the Type IV adsorption isotherm, which showed a relatively large pressure hysteresis region. This hysteresis is indicative of efficient adsorption, even for larger molecules, over an extended period.[22]

In brief, the BET analysis underscores the effectiveness of the activated carbon derived from spent coffee grounds and the CAA composite in wastewater treatment applications. The combination of a high surface area, microporosity, and a well-structured granular form makes this material an ideal candidate for adsorbing organic pollutants like MG from aqueous solutions.

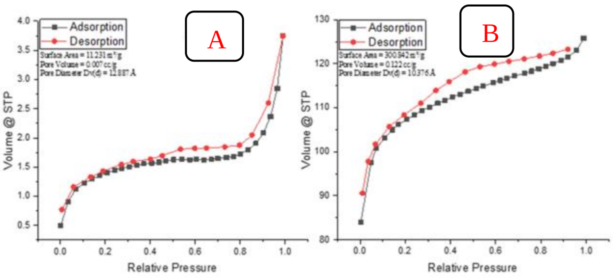

Figure 7. Adsorption/Desorption N_2 isotherm (BET equation) of CAA granular adsorbent (A); AC (B).

3.2.5. Point of zero charge of the CAA granular adsorbent

Understanding the point of zero charge (pH_{pzc}) is crucial for optimizing adsorption processes, especially in industrial and environmental applications like wastewater treatment. The pH_{pzc} represents the pH at which the adsorbent surface carries no net charge, meaning it neither attracts nor repels charged species from the solution. Below this pH, the adsorbent surface tends to be positively charged, while above it, the surface becomes negatively charged.[10] This property plays a significant role in how the material interacts with different pollutants in aqueous solutions.

In this study, the pH_{pzc} of the CAA adsorbent was determined to be 7.52, as shown in Figure 8. This isoelectric point, where the surface charge is neutral, marks a key threshold in the material's ability to adsorb different ions. Specifically, below a pH of 7.52, the material's surface is positively charged, making it more likely to attract anions. Conversely, when the pH rises above 7.52, the surface becomes negatively charged, favoring the adsorption of cations.

This finding is particularly significant for wastewater treatment applications. For example, the adsorption of MG, a cationic dye, is enhanced at pH values above 7.52, where the negative charge on the CAA surface attracts the positively charged dye molecules. This interaction promotes efficient adsorption of the dye, demonstrating how the pH_{pzc} plays a vital role in optimizing the removal of contaminants from wastewater.

The ability of the CAA material to efficiently adsorb both anions and cations at varying pH levels highlights its versatility as an eco-friendly adsorbent for wastewater treatment. By adjusting the pH of the solution, the adsorption efficiency of the material can be fine-tuned to target specific pollutants, providing a more adaptable and effective solution for real-world environmental applications. This underscores the significant impact of surface charge dynamics on the material's adsorption properties and its potential for treating wastewater in an eco-friendly and sustainable manner.

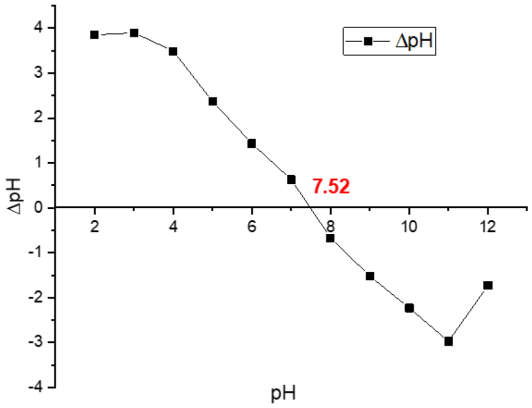

Figure 8. pH_{pzc} of granular adsorbent CAA.

The results presented in Figure 9 show that the adsorption efficiency and adsorption capacity increased significantly when the pH of the medium increased from 6 to 8.

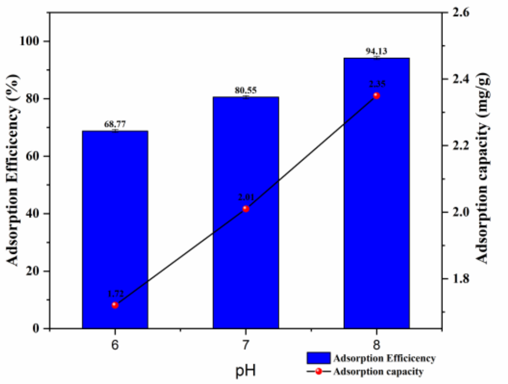

Figure 9. Effect of pH on the adsorption capacity of MG dye from aqueous solution of CAA adsorbent

Specifically, the adsorption efficiency increased from 68.77% to 94.13%, while the adsorption capacity increased from 1.72 mg/g to 2.35 mg/g. The pHpzc value was determined to be 7.52. The change in the surface properties of the material with pH can explain the mechanism of increased adsorption through both the surface charge and the protonation state of the active functional groups. At pH lower than the isoelectric point (pH < 7.52), the material surface is mainly positively charged because the functional groups such as the amine ($-NH_2$) of chitosan are protonated to $–NH_3^+$. As pH increases, the $–NH_3^+$ groups are gradually deprotonated back to $–NH_2$ (pKa ≈ 6.3–6.5), reducing the positive surface charge and increasing the ability to adsorb cations through coordination interactions or ion exchange.[23] At the same time, the -COOH groups on alginate and -OH groups on activated carbon begin to be deprotonated at pH > 4–5 (pKa of -COOH ≈ 3.5–4.5; pKa of -OH ≈ 9–10), resulting in an increasingly negative surface charge at pH > 7.5.[24] This facilitates the interaction with positively charged dye ions in solution.

4. CONCLUSION

This study successfully developed an eco-friendly granular adsorbent, CAA, by combining AC from spent coffee grounds with CS and AL. The adsorbent features a uniform size, rough surface, and well-developed capillary system, enhancing its adsorption potential. AC, prepared at 850 °C, showed a high degree of aromatic condensation, improving adsorption yield. The synthesis process was optimized with 3 g of AC, 0.75 M NaOH solution, 2% (w/v) AL concentration, and a 2-hour soaking period. FT-IR analysis confirmed successful integration of the components. The final adsorbent had an average diameter of 1.05±0.04 mm, specific surface area of 11.231 m²/g, and a pore diameter of 12.887 Å, making it ideal for dye removal. With a pH_{pzc} of 7.52, the CAA adsorbent demonstrates excellent potential for selectively adsorbing cationic dyes, such as MG, from wastewater. This study showcases the material's effectiveness and sustainability, offering a promising solution for environmentally-friendly wastewater treatment.

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