ENHANCED ADSORPTION OF METHYLENE BLUE USING CARBON-COATED MODIFIED VERMICULITE

TĂNG CƯỜNG KHẢ NĂNG HẤP PHỤ CHẤT MÀU METHYLENE BLUE BẰNG VERMICULITE BIẾN TÍNH PHỦ CARBON

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ABSTRACT

This study fabricated and evaluated carbon-coated modified vermiculite (CCMV) in methylene blue (MB) adsorption. The modification process involved thermal and chemical treatments to enhance surface area, porosity, and functional groups, thereby improving adsorption capacity. Batch experiments were conducted to assess the effects of initial dye concentration, contact time, pH, and temperature on MB removal efficiency. The results indicated that adsorption followed the Langmuir isotherm model and pseudo-second-order kinetics, characterized by monolayer adsorption and a chemisorption mechanism. Thermodynamic analysis confirmed that MB adsorption on CCMV was an endothermic process. With significantly higher adsorption performance compared to raw vermiculite, CCMV demonstrates strong potential for wastewater treatment applications involving dye pollutants. This study provides valuable insights into the development of modified clay-based materials for environmental treatments.

Keywords: *Carbon-coated vermiculite; methylene blue; adsorption; wastewater treatment.*

TÓM TẮT

Nghiên cứu này chế tạo và đánh giá vật liệu vermiculite biến tính phủ carbon (CCMV) trong hấp phụ methylene blue (MB). Quá trình biến tính bao gồm xử lý nhiệt và hóa học nhằm tăng diện tích bề mặt, độ xốp và nhóm chức năng, qua đó cải thiện khả năng hấp phụ của vật liệu. Các thử nghiệm hấp phụ theo mẻ đã được thực hiện để kiểm tra ảnh hưởng của nồng độ thuốc nhuộm ban đầu, thời gian tiếp xúc, độ pH và nhiệt độ đối với việc loại bỏ MB. Kết quả cho thấy hấp phụ tuân theo mô hình đẳng nhiệt Langmuir và động học giả bậc hai, phản ánh cơ chế hấp phụ đơn lớp và hấp phụ hóa học. Phân tích nhiệt động học cho thấy sự hấp phụ MB lên CCMV là thu nhiệt. CCMV thể hiện hiệu suất hấp phụ vượt trội so với vermiculite thô, từ đó khẳng định tiềm năng trở thành chất hấp phụ hiệu quả và thân thiện với môi trường trong xử lý nước thải chứa thuốc nhuộm. Nghiên cứu này cung cấp những hiểu biết quan trọng về sự phát triển của vật liệu trên cơ sở khoáng sét biến tính cho mục đích xử lý môi trường.

Từ khóa: *Vermiculite biến tính bọc carbon; methylene blue; hấp phụ; xử lý nước thải.*

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1. INTRODUCTION

Water pollution from industrial contaminants continues to be a significant global issue. Synthetic dyes, including methylene blue (MB), represent significant environmental and health hazards owing to their toxicity, persistence, and probable carcinogenic properties [1].

These dyes are extensively utilized in textiles, paper, and plastics, frequently released into aquatic systems without sufficient treatment. Consequently, the development of efficient, sustainable, and cost-effective adsorbents for dye removal has emerged as a critical research priority. Adsorption is acknowledged as one of the most efficient techniques for eliminating colors from wastewater owing to its simplicity, cost-effectiveness, and high removal efficacy [2]. Traditional adsorbents, including activated carbon, zeolites, and clay minerals, have been thoroughly examined for their adsorption properties [3, 4]. Nonetheless, the demand for enhanced adsorption capacity, regeneration potential, and environmental sustainability has prompted the investigation of innovative materials and surface changes.

Vermiculite, a naturally occurring layered silicate mineral, has garnered interest as a potential adsorbent owing to its elevated porosity, chemical stability, and cation exchange capacity [5, 6]. Nonetheless, its adsorption efficacy for organic pollutants, such as MB, is constrained by its comparatively modest surface area and diminished affinity for organic compounds [7]. To improve its adsorption efficacy, several surface modifications have been investigated, such as acid activation, metal impregnation, and carbon coating [8]. Carbon-coated materials exhibit considerable promise in environmental applications owing to their increased surface area, higher porosity, and functionalized surface groups that promote dye adsorption [9]. Carbon-based adsorbents, including biochar, activated carbon, and graphene, exhibit exceptional adsorption properties for organic contaminants, rendering them optimal for the modification of vermiculite. The addition of a carbon layer to vermiculite is anticipated to improve its dye removal efficacy by augmenting its surface functional groups, hydrophobic interactions, and electrostatic attraction to dye molecules.

This research investigates the adsorption of methylene blue (MB) by carbon-coated modified vermiculite (CCMV) made with biochar-derived carbon. It evaluates CCMV's physicochemical properties, adsorption efficiency under varying conditions (pH, contact time, dye concentration, temperature), and adsorption mechanisms using kinetic, isotherm, and thermodynamic models for wastewater treatment applications.

2. EXPERIMENTS

2.1. Chemicals

Vermiculite expanded 1:6 with H_2O_2 (30%), Chitosan, Methylene Blue (China).

2.2. Method of synthesis

Measure 0.5g of expanded Vermiculite 1:6 (EV) into a 100ml beaker holding 50ml of 1% Chitosan. Subsequently, immerse for 8 hours, stirring every 30 minutes to ensure uniform absorption of Chitosan on the EV surface, followed by baking at 700 °C for 1 hour. The acquired material is retained and utilized in subsequent studies.

2.3. Characterization

The expansion of vermiculite was assessed by measuring volume changes before and after expansion using a graduated measuring cylinder. The expansion coefficient (k) was calculated with k = V/V0. Phase analysis was performed using an X-ray diffractometer (X'Pert Pro) with a CuKα anode at a scanning rate of 5 °/min, in a 2θ range of 10° to 80°. Morphology was examined using scanning electron microscopy (SEM), and composition was analyzed with energy-dispersive X-ray spectroscopy (EDX). Porosity was determined via nitrogen gas adsorption (BET) at 77K, and thermal properties were evaluated through thermogravimetric analysis (TGA).

2.4. Adsorption capability of MB by CCMV

The absorption capacity of VER was evaluated using Methylene Blue at a concentration of 5ppm. The comprehensive experimental protocol is outlined as follows: Weigh approximately 0.05g of Chitosan-modified Vermiculite (EV-C), then fully submerge it in a 250ml conical flask containing 30ml of 5ppm Methylene Blue, followed by stirring, shaking, and allowing it to adsorb for 20 minutes. Subsequently, filter the adsorbent solution using a 0.22μm filter, and then quantify the adsorption using a UV-Vis spectrophotometer. Equilibrium adsorption capacity:

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

where q is the adsorption capacity (mg/g), C_o is initial solution concentration (ppm), C is solution concentration when reaching adsorption equilibrium (ppm) and V is solution volume (liter). Adsorbent adsorption capacity is crucial for practical application of the adsorption process and is measured empirically by the equilibrium capacity at a specific temperature as a function of concentration or duration. Modified VER (EV-C) was tested for Methylelene Blue adsorption by measuring the change in the fixed MB adsorbent concentration of 5ppm at 20 minutes using an adsorbent mass of 0.05g and a volume of 30ml. Adsorption isotherms were then created using the Langmuir and Freundlich models to assess the modified Vermiculite material's MB adsorption capability and estimate its maximum capacity.

Langmuir isotherm equation:

$$\frac{C_{cb}}{q} = \frac{1}{b.q_{max}} + \frac{1}{q_{max}}.C_{cb} \quad (2)$$

where q_{max} is the maximum adsorption capacity (mg/g), b is the Langmuir constant and C_{cb} is the concentration of adsorbed substance at equilibrium (ppm)

Freundlich isotherm equation:

$$\lg q = \lg k + \frac{1}{n}\lg C_{cb} \quad (3)$$

where q is the adsorption capacity, k is the constant depending on temperature, surface area,… and n is the constant depending on temperature (> 1).

MB adsorption kinetics were assessed by monitoring MB concentration changes over time with a 0.05g adsorbent mass and 30ml MB adsorbent volume. To determine how adsorption parameters affect reaction rate, first- and second-order kinetic equations were created.

First-order kinetic equation:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (4)$$

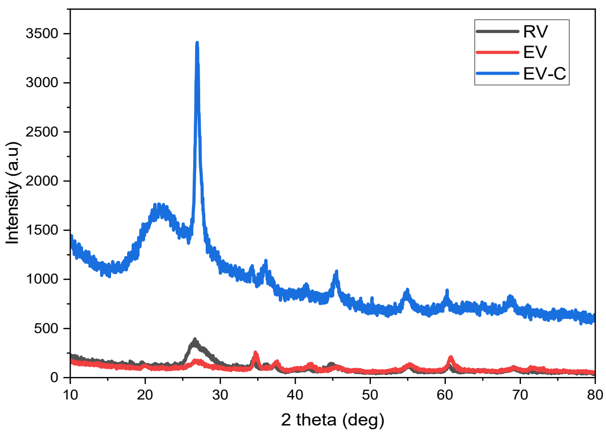
Second-order kinetic equation:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (5)$$

where q_t (mg/g) is the amount of adsorbent adsorbed at time t, q_e (mg/g) is the amount of adsorbent at equilibrium, k_1 (min^{-1} or s^{-1}) is the first-order adsorption rate constant, k_2 (g/mg.min) is the pseudo-second order adsorption rate constant and t is time.

3. RESULTS AND DISCUSSION

3.1. Characterization



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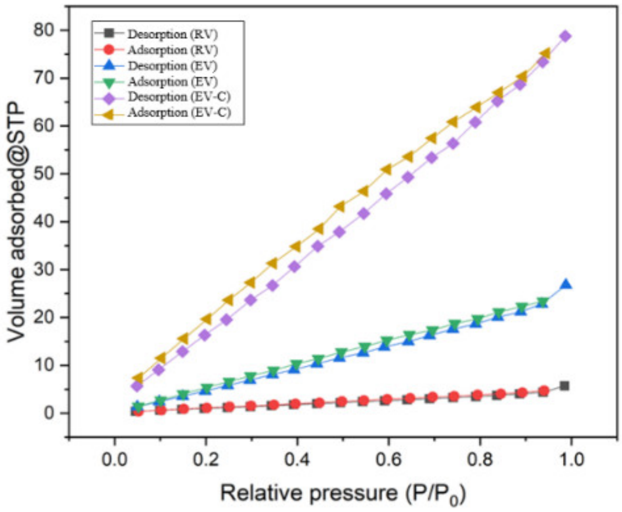
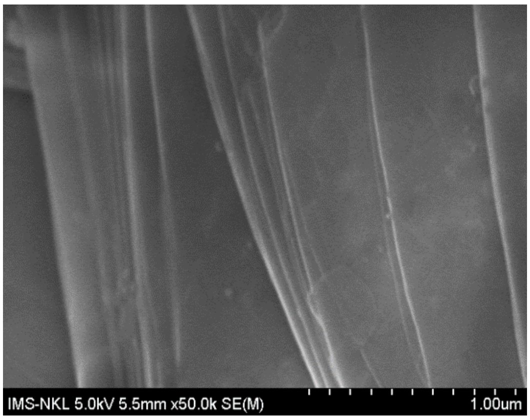


b)

Figure 1. X-ray diffraction patterns (a) and N_2 adsorption isotherm (b) of vermiculite before (RV), after expansion (EV) and modified (EV-C)

Figure 1 (a) shows XRD analysis of VER, revealing characteristic diffraction peaks at 2θ = 27.2° and 34.32°, with minor impurities indicated by weak peaks. A peak at 2θ = 26.5° confirms a carbon layer on the surface. Raw vermiculite (RV) has a distinct crystalline structure, while expanded vermiculite (EV) shows reduced peak intensity due to thermal expansion. Chitosan-modified vermiculite (EV-C) displays structural modifications enhancing adsorption. The BET surface area of RV is 5.943m^2/g, which increases to 36.970m^2/g for EV and 109.079m^2/g for EV-C, improving adsorption efficiency significantly.

Figure 2 presents SEM and optical microscope images of raw, expanded, and chitosan-modified vermiculite. The SEM image of raw vermiculite shows densely arranged, smooth layers, indicating an unexpanded state. Its sheet-like structure is evident in the optical image with a brownish-golden hue. Expanded vermiculite, as seen in both SEM and optical images, reveals a more porous, exfoliated structure, with a lighter, reflective color, indicating thermal treatment has separated its layers, enhancing its surface area for adsorption. Chitosan modification (c, g) further alters the surface texture, with SEM showing more roughness and fissures, suggesting interactions between chitosan and vermiculite. The chitosan-coated vermiculite has a deeper hue, likely from the organic coating. Overall, expansion increases the porosity and surface area, while chitosan modification improves surface properties, potentially boosting the vermiculite's adsorption capacity for contaminants like heavy metals. SEM provides detailed structural insights, while optical images highlight macroscopic changes.



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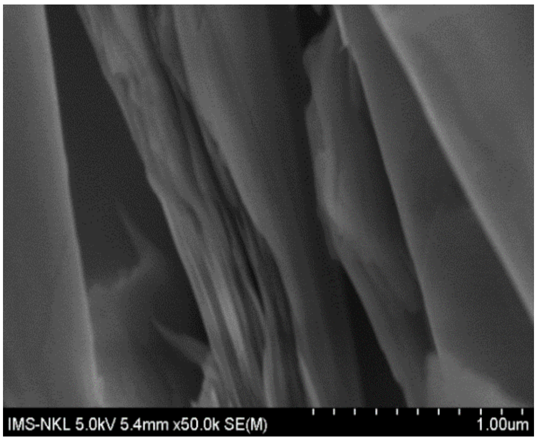

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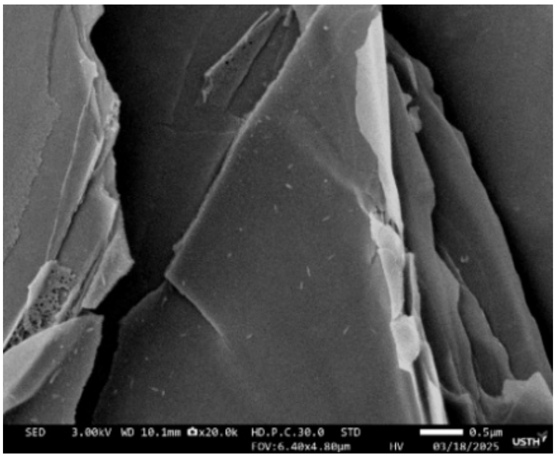
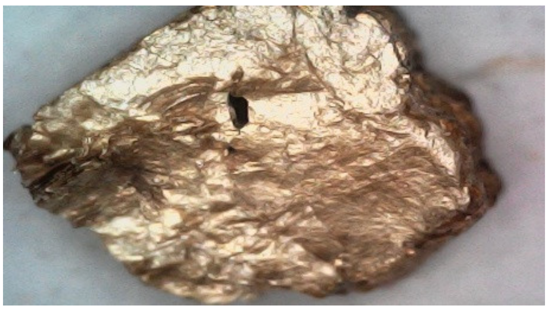


(c)



(d)

(e)

(g)

Figure 2. SEM and microscope images of raw vermiculite (a, d) expanded vermiculite (b, e) and vermiculite modified with chitosan (c, g)

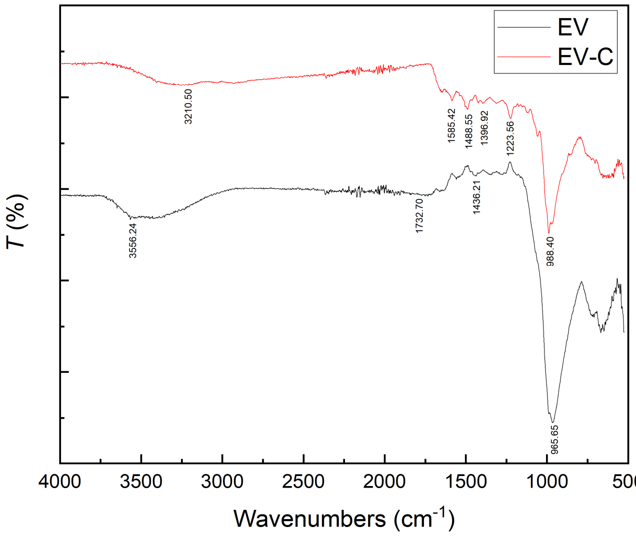


Figure 3. FTIR spectra of expanded vermiculite and vermiculite modified with chitosan

Figure 3 illustrates that the peak at approximately 3210cm^{-1} (-NH, -OH) confirms the existence of $-NH_2$ and -OH groups in chitosan. The peak at 1655cm^{-1} (C=O) of the amide is a distinctive indicator of the link between chitosan and vermiculite. The disappearance of the signal at 1732cm^{-1} (C=O) of carbonyl indicates a chemical alteration on the surface of vermiculite. The newly observed peaks at 1488 - 1396cm^{-1} (NH_3^+) and 1223cm^{-1} (C-N) have validated the presence of chitosan on the vermiculite surface. The Si-O vibration (1000 - 5000cm^{-1}) stays unchanged, indicating that the fundamental structure of vermiculite has not been compromised but merely altered on the surface. The FTIR data indicate that the modification of vermiculite with chitosan has generated new functional groups, hence improving adsorption capacity and confirming the efficacy of the modification procedure.

Figure 4 illustrates that prior to modification with chitosan, the zeta potential of EV was -63.8mV. Following modification, the zeta potential of EV-C was -20.3mV, indicating that the surface of vermiculite experienced partial neutralization of its negative charge due to the positively charged nature of chitosan. The modification with chitosan enhanced the material's aggregation in water, hence enhancing the adsorption of negatively charged entities such as colors or metals.

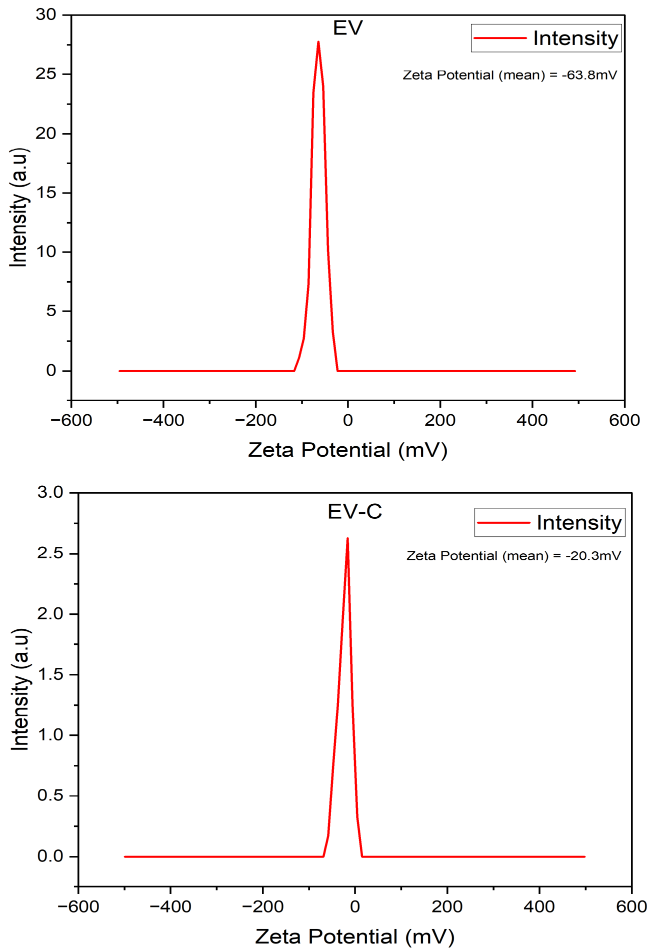


Figure 4. The zeta potential of Expanded Vermiculite; Vermiculite material modified with Chitosan

The EDX spectrum of EV-C in Figure 5 indicates the presence of predominant elements, with O (34.6%) representing the greatest proportion, primarily derived from mineral oxides in vermiculite, including SiO_2, Al_2O_3, and Fe_2O_3. Si (13.0%) is the principal component of vermiculite, Mg (6.2%) is a significant component of vermiculite, and Al (5.5%) is present as aluminum oxide. The existence of the aforementioned aspects demonstrates that the configuration of EV-C is appropriate. The sample contains chitosan, evidenced by a substantial Carbon content of 11.2%, indicating the successful modification process, with chitosan attached to the surface of vermiculite.

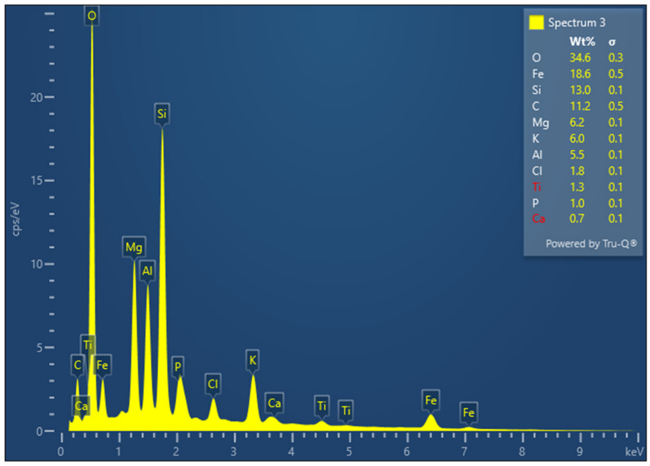


Figure 5. EDX spectra of vermiculite modified with chitosan

3.2. Adsorption capability of MB by CCMV

Figure 6 illustrates that the adsorption effectiveness of MB progressively diminishes as MB concentration increases. As the concentration rises, indicating an increase in the MB dye component within the solution, the fixed quantity of 0.05g of vermiculite will be insufficient to adsorb all MB elements, as the capillaries of the modified Vermiculite become saturated. Specifically, when the solution concentration ranges from 5ppm to 40ppm, and modified vermiculite is utilized for a constant duration of 20 minutes, the best effectiveness is observed at an MB content of 5ppm.

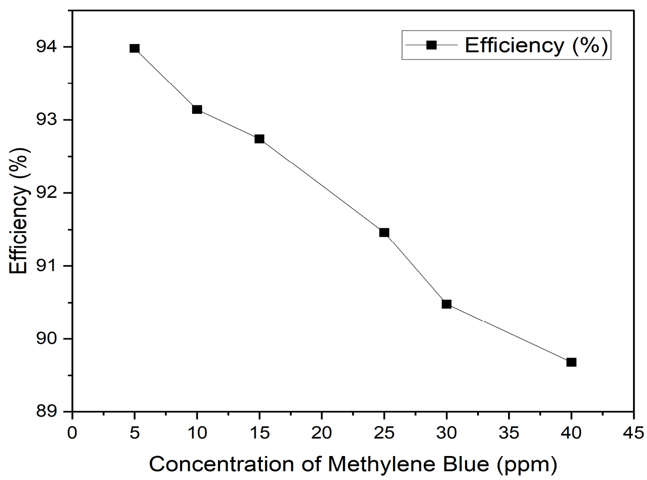


Figure 6. Efficiency of MB adsorption on vermiculite modified with chitosan

The adsorption of MB by chitosan-modified vermiculite was characterized as monolayer adsorption, governed by a homogenous process, with a maximum adsorption capacity of 45.05mg/g and a Langmuir constant (b) of 0.21. The findings from the two adsorption isotherm equations in Figure 7 indicate that the Freundlich isotherm model more precisely characterizes the adsorption of MB onto modified Vermiculite than the Langmuir model, as seen by its superior correlation coefficient R^2 (0.9976 > 0.9792). The coefficient n = 1.29 (1 < n < 10) is advantageous for the adsorption process. Consequently, the Freundlich isotherm adsorption model more accurately characterizes the MB adsorption process of EV-C compared to the Langmuir model.

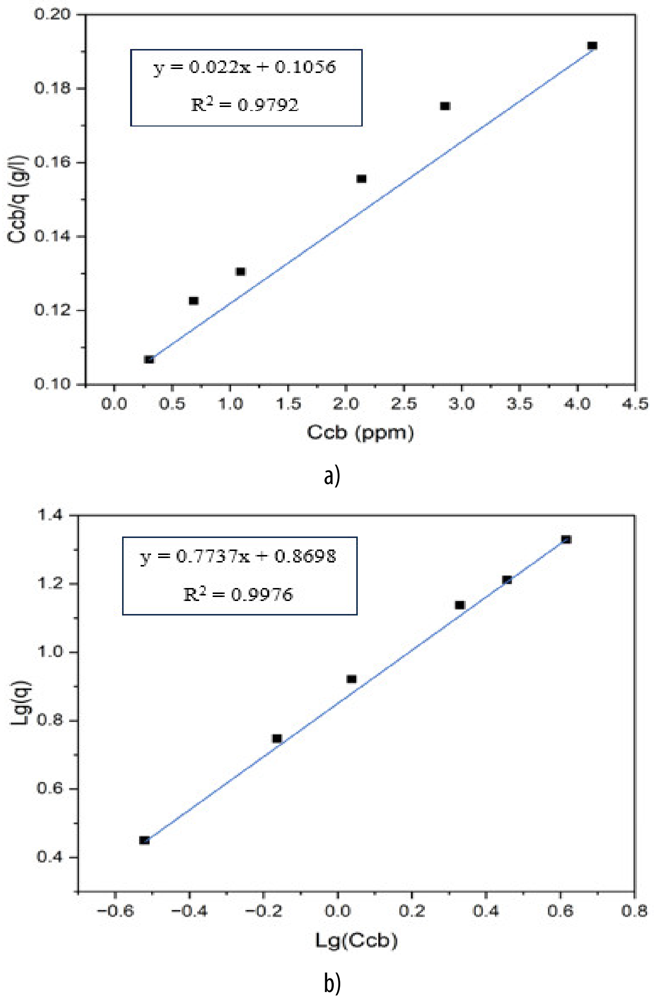


Figure 7. The isotherm and linear of Langmuir (a) and Freundlich (b) model for MB adsorption on the vermiculite modified with chitosan

The adsorption study of Methylene Blue on modified Vermiculite shows that after 40 minutes, the adsorption capacity reaches equilibrium at qe = 2.9042mg/g. The pseudo-first-order kinetic model gives a correlation coefficient R^2 = 0.9440 and a rate constant k_1 = 0.0745 min^{-1}. However, the second-order kinetic model is more suitable, with an equilibrium capacity of qe = 2.8653mg/g, a rate constant k_2 = 0.7106, and a higher R^2 = 0.9998. This higher correlation coefficient indicates that the adsorption process follows the second-order kinetic model, which is more effective in describing the adsorption of Methylene Blue.

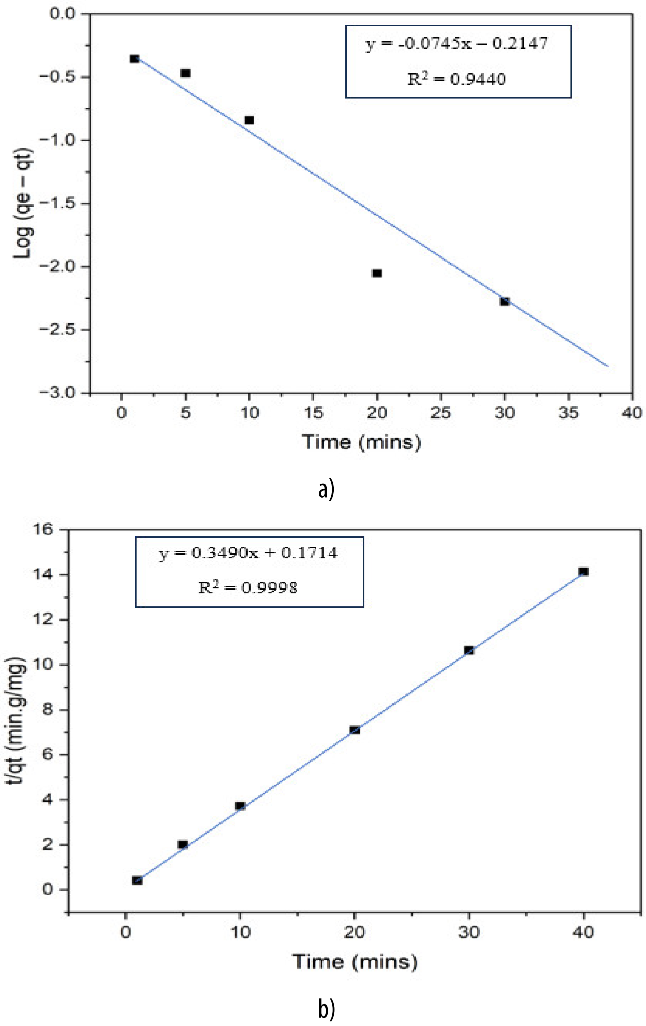


Figure 8. MB adsorption linear plot with pseudo-first-order (a) and pseudo-second-order (b) kinetic models on the vermiculite modified with chitosan

According to the Langmuir model, Chitosan-modified vermiculite stands out as the most promising adsorbent material among those studied. Report in Table 1 shown with a q_{max} of 45.05mg/g, it not only exhibits superior adsorption efficiency but also combines the benefits of two widely used components: vermiculite (affordable and abundant) and chitosan (natural and eco-friendly). This makes it a strong candidate for real-world applications in wastewater treatment, especially for removing dye pollutants like methylene blue.

Table 1. The adsorption capacity of various adsorbents for the MB dye

Adsorbent	Methylene Blue adsorption capacity, mg/g	References
Biochar prepared from jackfruit peel	39.87	[10]
Biochar Derived from Mimosa Pigra Plant	20.18	[10, 11]
The chitosan bead material has a porous structure	7.25	[10, 12]
Magnesium-Modified Fly Ash (Mg@FA)	14.34	[12, 13]
Walnut shell-activated carbon	3.53	[10, 13]
Biochar prepared from date palm seeds	40.76	[14]
Bentonite Clay	27.93	[13, 15]
Ecuadorian Red clays were combined with precursor clays and the $ZnTiO_3/TiO_2$ semiconductor	36.24	[13]
Chitosan-modified vermiculite	45.05	This study

3.3. Recyclability of chitosan-modified vermiculite for Methylene Blue

Regenerating the adsorbent is vital for the sustainability of the adsorption process. Replacing the adsorbent is costlier than reusing it, so its reusability is crucial. For desorbing Methylene Blue (MB) from chitosan-modified vermiculite (EV-C), EtOH solutions were tested. Figure 9 shows that after the first regeneration, removal efficiencies were 93.98%, 86.88%, 84.22%, 83.85%, and 83.44%. The efficiency dropped from 93.98% in the first cycle to 86.88% and 84.22% in the subsequent cycles but stabilized from the third cycle onward. This indicates that EtOH is the most effective desorbing agent for MB removal from modified vermiculite.

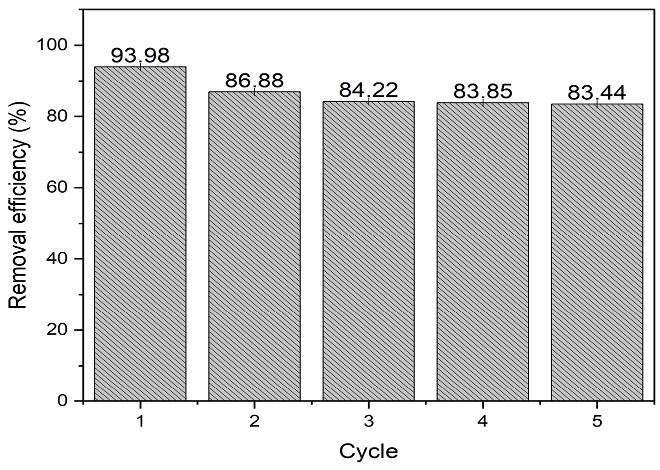


Figure 9. The reusability of modified vermiculite as adsorbent for the removal of MB

4. CONCLUSION

Using a concentration of 1% chitosan that was soaked for eight hours and then calcined at 700°C, the expanded vermiculite material that had been modified with chitosan was effectively investigated. The method of calcination in an inert atmosphere was successfully utilized. In comparison to the original vermiculite and the enlarged vermiculite, the modified vermiculite exhibited a higher capacity for adsorbing methylene blue. This was due to the fact that the modified vermiculite had a bigger surface area than both the original vermiculite and the expanded vermiculite simultaneously. According to these findings, the enlarged vermiculite that was investigated using the method of modification with chitosan in conjunction with the calcination process inside of an inert atmosphere will be a prospective and promising adsorbent that can assist in the treatment of various hazardous compounds that are found in the environment.

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