Research

Evaluation of nitrate removal efficiency from aqueous solutions using modified biochar derived from coffee husk

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ABSTRACT

This study presents the fabrication and evaluation of the nitrate adsorption capacity of modified biochar derived from coffee husk. The coffee husks were initially pyrolyzed at 350 °C for 1 hour, then soaked in 1 M KOH solution for 24 hours, followed by a second pyrolysis step at 700 °C for 2 hours. The resulting biochar was characterized using FT-IR, BET, and SEM techniques, and its nitrate removal efficiency from aqueous solutions was investigated. The highest nitrate removal efficiency (82,38%) was achieved under the following conditions: pH 3, biochar dosage of 1,5 g/100 mL, nitrate concentration of 50 mg/L, and reaction time of 210 minutes. The pseudo-first-order kinetic model and the Langmuir isotherm model were applied to describe the adsorption behavior, showing good agreement with the experimental data.

Keywords: Adsorption; Biochar; Coffee husk; Nitrate $(NO_3^-)^-$

1. INTRODUCTION

Nitrate (NO_3^-) is a stable and mobile anion commonly found in various environmental media. Once ingested, it can be reduced to nitrite by gut bacteria, which poses health risks due to its ability to convert hemoglobin into methemoglobin, impairing oxygen transport. This condition, methemoglobinemia, is especially dangerous for infants under six months. Additionally, nitrite can form carcinogenic N-nitroso compounds through reactions with endogenous amines [1, 2]. Due to its high solubility and persistence, nitrate contamination is widespread in surface water, groundwater, and wastewater [3]. Various removal methods exist, such as ion exchange, reverse osmosis, biological denitrification, and adsorption [4, 5]. Among natural materials, studies focus mainly on adsorption using carbon-based materials (e.g., biochar) and biological transformation by microorganisms, algae, or fungi [6-8]. Biochar stands out for its stability, ease of handling, and ability to be produced from low-cost agricultural residues without the need for strict cultivation conditions. It also avoids biological sludge production and can serve as a microbial support medium, making it suitable for integrated treatment systems.

Vietnam, a major global coffee producer, generates over 600,000 tons of coffee husks annually as a by-product of coffee processing [9]. These husks are often underutilized, offering a promising opportunity for conversion into value-added, eco-friendly adsorbents. In this study, we synthesized activated carbon from coffee husks via a two-step chemical activation method. This approach was selected for its ability to produce materials with high carbon content, large surface area, and enhanced porosity, which are critical for effective nitrate adsorption [10].

2. MATERIALS AND METHOD

2.1. Preparation of modified biochar as an adsorbent

Biochar (BC) was synthesized from coffee husk through pyrolysis under limited air conditions using a non-circulating muffle furnace, as described in previous studies [11]. Initially, the coffee husks were thoroughly washed and air-dried, then packed into a lidded ceramic crucible and subjected to pyrolysis at 350 °C for 60 minutes. The resulting biochar (referred to as BC) was subsequently modified via a wet chemical activation method using 1 M KOH. Specifically, 10 g of BC was mixed with 200 mL of KOH 1M solution and stirred for 24 hours. The mixture was then dried at 105 °C for 3 hours. A second pyrolysis step was carried out at 700 °C for 2 hours. After pyrolysis, the product was thoroughly washed with RO (reverse osmosis) water until the pH, as measured by pH paper, reached neutral (pH = 7). The final modified biochar was oven-dried at 105 °C for 3 hours, cooled to room temperature, and stored in clean, airtight containers. The overall fabrication process of modified biochar from coffee husk is illustrated in figure 1 below:

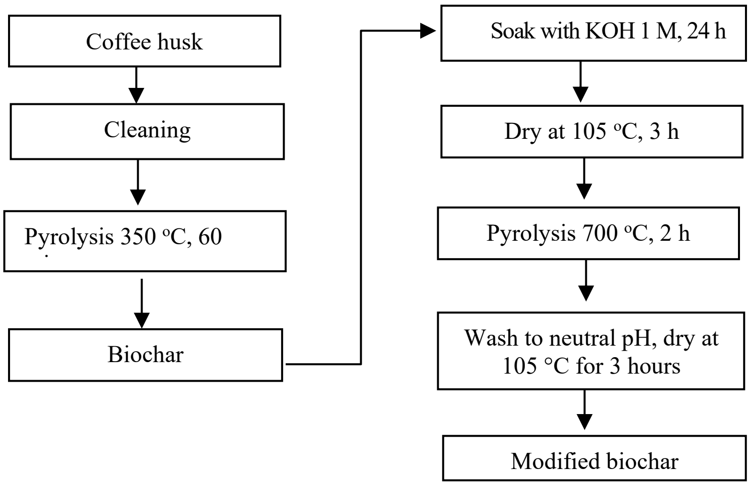


Figure 1. *Process of synthesizing modified biochar from coffee husk.*

The images of the modified biochar are presented in figure 2 below:

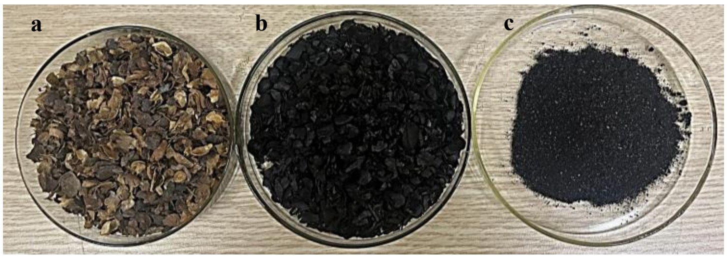


Figure 2. *Modified biochar from coffee husk:*
a) Coffee husk; b) After pyrolysis; c) After modification.

The two-step process was selected to optimize the porous structure and enhance the adsorption efficiency of biochar derived from coffee husks. In stage 1 - pyrolysis, dehydration and partial decomposition of organic compounds occur, while the release of CO_2 gas promotes the initial development of pores. This increases the surface area of the material and improves its interaction with KOH in the following stage (yield: 56,7%).

In stage 2 - chemical activation with KOH, carbon in the biochar reacts with KOH to form K_2CO_3 (reaction 1), while any remaining hemicellulose and lignin are further decomposed. Upon heating at 700 °C, K_2CO_3 decomposes into CO and CO_2 (reactions 2, 3, 4), which further expands the pore network within the material.

$$6\ KOH + 2\ C \rightarrow 2\ K + 2\ K_2CO_3 + 3\ H_2 \qquad (1)$$

$$K_2CO_3 \rightarrow K_2O + CO_2 \qquad (2)$$

$$K_2CO_3 + 2\,C \rightarrow 2\,K \text{ (hoặc } K_2O) + 3\,CO \quad (3)$$
$$K_2O + C \rightarrow 2\,K + CO \quad (4)$$

The yield after activation was 59,3%, and the overall yield of the process reached 33,6%. This method enables the near-complete mineralization of the material, thereby significantly reducing the potential for organic contamination in tap water treatment applications.

2.2. Modified biochar characterization

The functional groups and characteristic bonds of the modified biochar (BC) were identified using Fourier-transform infrared spectroscopy (FT-IR) on a Tensor II device (Bruker, Germany) at the Institute of Chemistry and Materials. The surface morphology of the modified BC was evaluated using scanning electron microscopy (SEM) on a JSM-6510LV microscope (Jeol, Japan) at the Institute of Tropical Engineering, Vietnam Academy of Science and Technology. The specific surface area was determined using the Brunauer–Emmett–Teller (BET) method on an ASAP 2060 instrument (Micromeritics, USA) at Hanoi University of Science and Technology.

Determination of the Point of Zero Charge (pHpzc): A 0,1 M NaCl solution was prepared, and 0,1 M NaOH and 0,1 M HCl were used to adjust the initial pH (pHi) of the solution, varying from 2 to 12. Modified biochar (0,5 g) was weighed into screw-cap glass bottles, and 50 mL of the pH-adjusted 0,1 M NaCl solution was added. The mixture was agitated on a horizontal shaker for 24 hours at room temperature, followed by filtration through Whatman 0,45 µm filter paper to remove the biochar. The final pH (pHf) was measured, and the pH difference (ΔpH = pHf - pHi) was calculated. The point where the ΔpH curve intersects the initial pH (pHi) corresponds to the point of zero charge (pHpzc) of the modified biochar.

2.3. Nitrate adsorption in modified biochar

The experiment was conducted at room temperature using a 250 mL Erlenmeyer flask containing 100 mL of nitrate (NO_3^-) solution at a concentration of 50 mg/L (as N) and 0,5 g of modified biochar material. The mixture was stirred at 300 rpm. After the adsorption period, the sample was filtered using Whatman filter paper with a pore size of 0,45 µm to separate the biochar. The residual NO_3^- concentration in the solution was determined by a colorimetric method using a UV-Vis spectrophotometer**.**

2.3.1. Effect of pH

The pH of the solution was adjusted in the range of 1 to 9 using either 0,1 N NaOH or 0,1 N H_2SO_4. After 120 minutes of adsorption, the samples were filtered and analyzed for residual NO_3^- concentration. The nitrate removal efficiency was calculated using the following equation:

$$H = \frac{Co - Ct}{Co}\, x\, 100\%$$

where C_0 is the initial concentration and C_t is the NO_3^- concentration at time *t*.

2.3.2. Effect of reaction time

The effect of reaction time was investigated at intervals of 30, 60, 90, 120, 150, 180, and 210 minutes. The solution pH was adjusted to the optimal value determined in experiment (a). The NO_3^- concentration, the ratio of modified biochar to NO_3^- solution, and other experimental conditions were maintained as previously described. Pseudo-first-order and pseudo-second-order kinetic models were employed to evaluate the adsorption kinetics of NO_3^- from aqueous solution by the modified biochar.

Pseudo-first-order:

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

Pseudo-second-order:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$$

Where, k_1 (min^{-1}) is the rate constant of the adsorption process of the first-order reaction; k_2 (g/mg.min) is the rate constant of the adsorption process of the second-order reaction; q_e (mg/g) s the adsorption capacity at equilibrium; q_t (mg/g) is the adsorption capacity at time t.

2.3.3. Effect of modified biochar dosage

The influence of the modified biochar dosage was examined by varying the amount of adsorbent at 0,05; 0,5; 1,0; 1,5; and 2,0 g per 100 mL of NO_3^- solution at a concentration of 50 mg/L. The optimal pH and contact time determined in experiments (a) and (b) were applied. The Langmuir and the Freundlich isotherm models were employed to evaluate the equilibrium adsorption behavior of NO_3^- onto the modified biochar in aqueous solution.

Langmuir adsorption isotherm equation:

$$\frac{C_e}{q_e} = \left(\frac{1}{q_{max}}\right) C_e + \frac{1}{q_{max} K_L}$$

Freundlich adsorption isotherm equation:

$$\ln(q_e) = \ln(K_F) + \frac{1}{n} \ln{(C_e)}$$

Where, q_e (mg/g) is the adsorption capacity at equilibrium, C_e (mg/L) is the adsorbate concentration at equilibrium, q_{max} (mg/g) is the maximum saturated monolayer adsorption capacity of an adsorbent, K_L (L/mg) is the Langmuir constant, K_F (L/mg) is the Freundlich constant, n is adsorption intensity parameter.

2.3.4. Calibration curve for NO_3^- determination

The calibration curve for NO_3^- analysis in the concentration range of 0,5 - 20 mg/L was established according to TCVN 7323-1:2004. The resulting calibration equation was y = 0,0663x - 0,0068, $R^2 = 0,9995$.

3. RESULTS AND DISCUSSIONS

3.1. Results of material preparation

3.1.1. FT-IR Spectrum of modified biochar

The IR spectra of the biochar sample before and after modification with KOH are shown in figure 3.

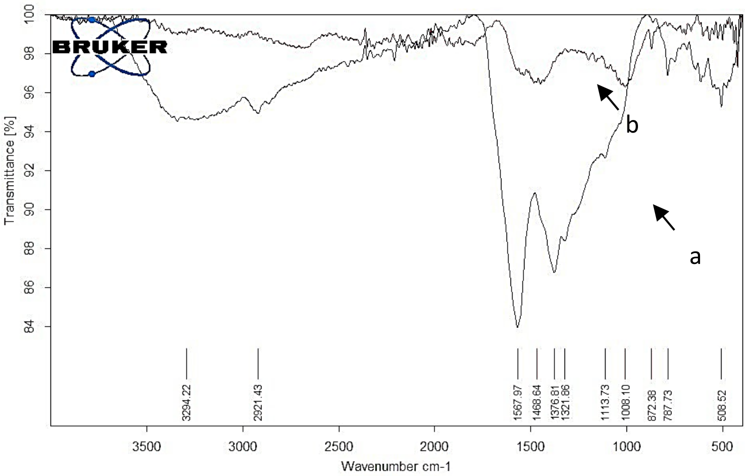
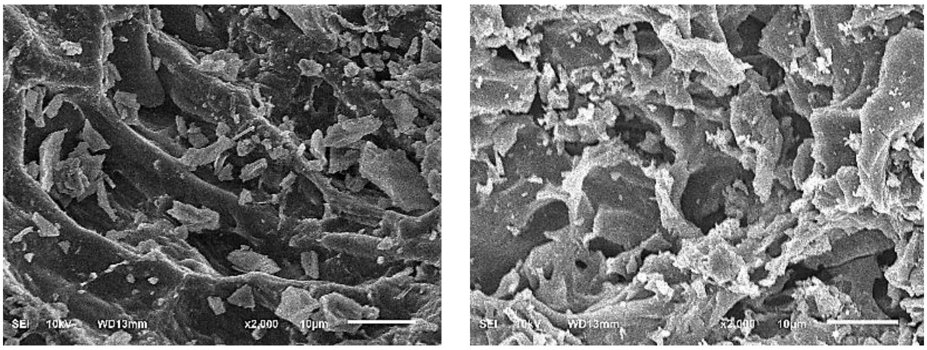


Figure 3. *FT-IR spectra of unmodified (a) and modified biochar (b).*

The IR spectra exhibit absorption peaks characteristic of functional groups and bonds present in biochar. The absorption peak at 3294 cm^{-1} is attributed to the stretching vibration of the -OH group, while the peak at 2921 cm^{-1} corresponds to the stretching vibration of the -CH (aliphatic) bond. An absorption peak at 1567 cm^{-1} is characteristic of the stretching vibration of the C=C bond in the aromatic ring, which is further confirmed by the out-of-plane bending vibration of the =CH bond in the aromatic ring at 787 cm^{-1}. The absorption peak at 1376 cm^{-1} is attributed to the stretching vibration of the CO_3^{2-} group, which forms during the modification process. In the IR spectrum of the modified biochar, the absorption peaks characteristic of organic compounds are no longer present. Therefore, when modified biochar is used for water treatment, it will not pose a risk of secondary contamination through the leaching of organic substances from the adsorbent material.

3.1.2. Morphology of modified biochar

The morphology of biochar before and after modification with KOH 1M is illustrated by the SEM images in figure 4. The surface of unmodified biochar shows numerous small fragments, with a sparse and poorly defined porous structure. In contrast, the surface of the modified biochar exhibits a significantly higher number of pores. This is attributed to the reaction between the carbon in biochar and KOH, resulting in the formation of K_2CO_3. During the thermal treatment at 700 °C, K_2CO_3 further decomposes, releasing CO_2 and generating additional pores. As a result, the modified biochar shows a more developed and porous structure compared to the unmodified material.



Unmodified biochar *Modified biochar*

***Figure 4**. SEM image of unmodified and modified biochar.*

The specific surface area (BET) of the biochar samples before and after modification was measured. As shown in table 1, the biochar modified with KOH 1M exhibited a specific surface area of 383,64 m^2/g, higher than biochar before modification (336,256 m^2/g), the micro pore volume of the modified biochar was 0,789 cm^3/g, five times greater than unmodified biochar (0,157 cm^3/g). Pore size has a significant impact on the accessibility of the biochar surface to the adsorbed substances. Moreover, the number of micropores is positively correlated with the surface area of the biochar. Therefore, the more micropores present on the surface, the larger the surface area, which facilitates easier access for molecules and accelerates the adsorption process.

***Table 1.** BET results of unmodified and modified biochar.*

Material	Before modification	After modification with KOH 1M
BET surface area, m^2/g	336,256	383,638
Langmuir surface area, m^2/g	485,906	538,188
Micro pore volume, cm^3/g	0,157	0,789

3.1.3. Determination of the point of zero charge (pHpzc)

The point of zero charge (pHpzc) refers to the pH at which the surface of the adsorbent is electrically neutral. When the pH is lower than the pHpzc, the adsorbent surface carries a positive charge, thereby favoring the adsorption of anions. Conversely, when the pH exceeds the pHpzc, the surface becomes negatively charged, enhancing the adsorption of cations. The result indicates that the modified biochar exhibits a pHpzc value of 3,71 (figure 5).

3.2. Evaluation of nitrate removal efficiency using modified biochar

3.2.1. Effect of pH on nitrate removal efficiency

pH is a critical parameter influencing the efficiency of NO_3^- removal from aqueous solutions. The impact of pH on the NO_3^- removal performance of modified biochar is illustrated in figure 6:

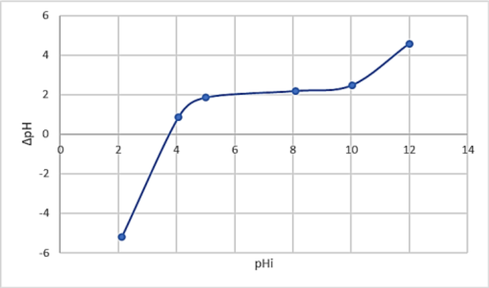


Figure 5. *pHpzc of modified biochar.*

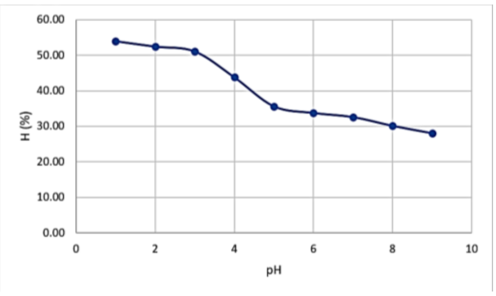


Figure 6. *Effect of pH on NO_3^- removal efficiency.*

As shown in figure 6, the highest removal efficiency (53,88%) was achieved at pH = 1. This can be attributed to the fact that at pH values lower than the point of zero charge (pHpzc = 3,71), the surface of modified biochar is positively charged, which facilitates the attraction and adsorption of negatively charged NO_3^- ions. As the pH increases from 1 to 3, the removal efficiency decreases slightly by approximately 5%, indicating minimal variation. However, a marked decrease in removal efficiency is observed as pH continues to rise from 3 to 9 (43,77% to 28,08%, respectively). At high pH levels, the nitrate adsorption capacity of biochar decreased due to the competition between NO_3^- and OH^- ions [12]. At low pH, the biochar surface carries a positive charge (due to the accumulation of H^+ ions), which enhances the electrostatic attraction between H^+ ions on the surface and NO_3^- ions [12]. Similar results were also reported in the study by Viglašová et al. (2018) [13]. To optimize chemical usage in practical applications, a pH of 3 was selected for subsequent experiments.

3.2.2. Effect of reaction time on nitrate removal efficiency

The influence of reaction time on NO_3^- removal efficiency at pH = 3 is presented in figure 7.

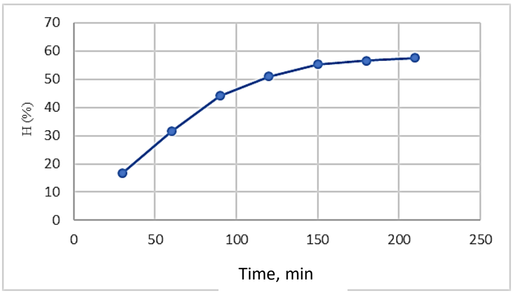


Figure 7. *Effect of contact time on NO_3^- removal efficiency.*

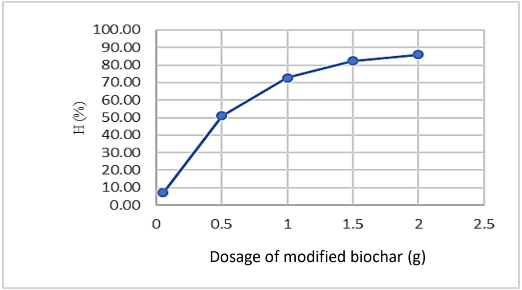


Figure 8. *Effect of adsorbent dosage on NO_3^- removal efficiency.*

As shown in figure 7, the removal efficiency increases proportionally with contact time. When the contact time increased from 30 to 210 minutes, NO_3^- removal improved from 16,77% to 57,65%. Therefore, the optimal contact time for subsequent experiments was set at 210 minutes.

3.2.3. Effect of adsorbent dosage on nitrate removal efficiency

Figure 8 illustrates the effect of varying the mass of modified biochar from 0,05 g to 2,0 g on NO_3^- removal. The removal efficiency increased significantly from 7,12% to 86,0%. A plateau was observed beyond 1,5 g, with efficiencies of 82,38% and 86,0% for 1,5 g and 2,0 g, respectively. This can be explained by the fact that increasing the amount of biochar increases the number of available adsorption sites on its surface, thereby enhancing the binding with NO_3^- ions and resulting in higher nitrate adsorption efficiency. It can be concluded that the amount of adsorbent material is directly proportional to the adsorption efficiency. Thus, 1,5 g of modified biochar was selected for further studies to balance cost and performance.

3.3. Kinetic modeling of NO_3^- adsorption onto modified biochar

The NO_3^- adsorption kinetics were evaluated using pseudo-first-order and pseudo-second-order models, as shown in figure 9:

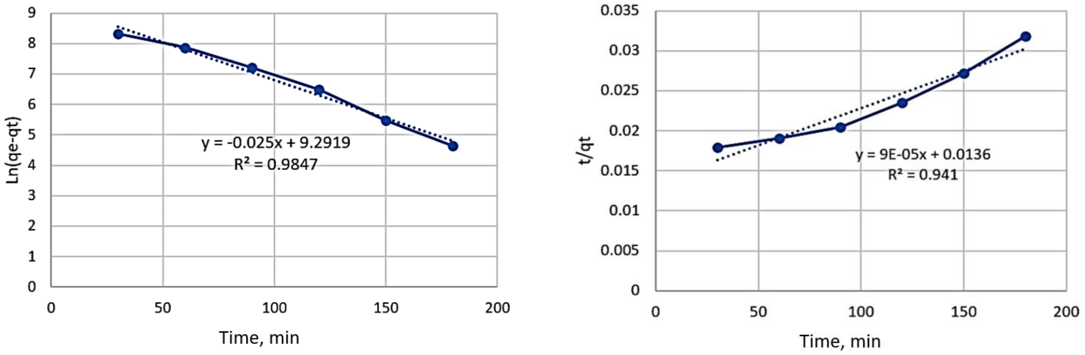


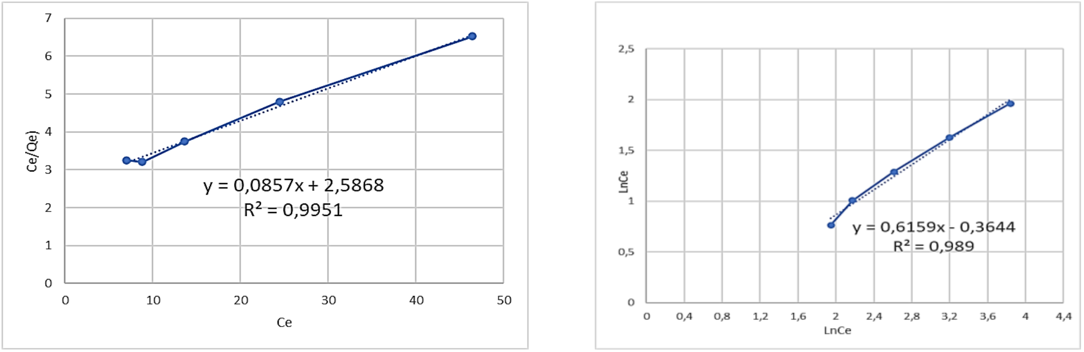
Figure 9. *Pseudo-first-order kinetics (left) and pseudo-second-order kinetics (right).*

Table 2. *Kinetic and isotherm model parameters for NO_3^- adsorption.*

<table>
<tr><td colspan="4">Pseudo-first-order</td><td colspan="4">Pseudo-second-order</td></tr>
<tr><td>R^2</td><td>k_1</td><td>$q_{e.cal}$</td><td>$q_{e.exp}$</td><td>R^2</td><td>k_2</td><td>$q_{e.cal}$</td><td>$q_{e.exp}$</td></tr>
<tr><td>0,9847</td><td>0,025</td><td>5,390</td><td>5,764</td><td>0,941</td><td>$6,3 \times 10^{-4}$</td><td>10,810</td><td>5,764</td></tr>
<tr><td colspan="4">Langmuir isotherm model</td><td colspan="4">Freundlich isotherm model</td></tr>
<tr><td>R^2</td><td>K_L</td><td colspan="2">R_L</td><td>R^2</td><td>K_F</td><td colspan="2">1/n</td></tr>
<tr><td>0,9951</td><td>0,033</td><td colspan="2">0,377</td><td>0,9890</td><td>0,690</td><td colspan="2">0,610</td></tr>
</table>

These results suggest that the NO_3^- adsorption process is best described by the pseudo-first-order model, with a higher R^2 value (0,9847) compared to the pseudo-second-order model (0,9410). Additionally, the calculated $q_{e.cal}$ value closely matched the experimental value.

To assess the dependence of adsorption capacity on NO_3^- concentration, isotherm models were fitted using the experimental data. The Langmuir and the Freundlich isotherms are presented in figure 10, and their parameters are summarized in table 2. Both models adequately described the adsorption behavior, with R^2 values close to 1 and parameters R_L and 1/n within the favorable range of 0 to 1. However, the Langmuir model demonstrated a slightly better fit to the experimental data (R^2 = 0,9951), indicating monolayer adsorption on a homogeneous surface.



a) *b)*

Hình 10. *Langmuir isotherm (a) and Freundlich isotherm (b).*

4. CONCLUSIONS

A modified biochar adsorbent was successfully synthesized from coffee husk via a two-step pyrolysis method using KOH 1M. The material exhibited a high specific surface area (383,838 m^2/g) and an average pore size of 6,219 Å. The modified biochar demonstrated effective NO_3^- removal performance, achieving an optimal removal efficiency of 82,38% under conditions of pH 3, 210 minutes reaction time, and an adsorbent dosage of 1,5 g per 100 mL of 50 mg/L NO_3^- solution. Adsorption kinetics followed the pseudo-first-order model, while equilibrium data fitted both the Langmuir and the Freundlich isotherms, with Langmuir providing a better representation. The maximum adsorption capacity of the modified biochar for NO_3^- was determined to be 11,66 mg/g.

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TÓM TẮT

Nghiên cứu đánh giá hiệu quả xử lý nitrate trong nước
của than sinh học biến tính chế tạo từ vỏ cà phê

Bài báo này giới thiệu kết quả nghiên cứu chế tạo và đánh giá khả năng hấp phụ nitrate trong nước của than sinh học biến tính chế tạo từ vỏ cà phê. Vỏ cà phê được nhiệt phân ở 350 °C, 1 h, sau đó ngâm với KOH 1 M trong 24 h, nhiệt phân tiếp ở 700 °C trong 2 h. Sản phẩm sau chế tạo được đánh giá đặc tính bằng FT-IR, BET, SEM và khảo sát hiệu quả xử lý nitrate trong nước. Tại pH = 3, tỷ lệ than 1,5 g/100 mL dung dịch NO_3^- 50 mg/L, thời gian hấp phụ 210 min cho hiệu quả xử lý nitrate đạt cao nhất (82,38%). Mô hình động học biểu kiến bậc 1 và mô hình hấp phụ đẳng nhiệt Langmuir đã được xem xét và co thấy sự phù hợp để mô tả quá trình hấp phụ của than sinh học biến tính.

Từ khóa: Hấp phụ; Than sinh học; Vỏ cà phê; NO_3^-.