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Biochar of post-extraction coffee bean ground as materials for ammonium adsorption

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Abstract. The presence of ammonium in drinking water poses a significant global challenge, demanding strategies that safeguard both public health and the environment. By exploring the potential of coffee processing byproducts, this research seeks to contribute to the development of sustainable and efficient solutions for mitigating ammonium contamination in groundwater. This study investigates the adsorption potential of AC-GCB biochar, obtained by pyrolyzing green coffee extracted bioactive compounds at 400 ºC, for ammonium removal from groundwater. The biochar's microstructure was characterized using scanning electron microscope (SEM), Fourier-transform infrared spectroscopy (FTIR), and Energy dispersive spectrometry (EDS) Mapping. Optimal adsorption conditions were observed at an initial pH range of 4 to 8, an initial NH_4^+ concentration of ≤ 25 $mg.L^{-1}$, and a biochar dose of 10 $g.L^{-1}$. The ammonium adsorption of AC-GCB was consistent with both Langmuir and Freundlich's adsorption theories ($R^2 > 0.92$). The AC-GCB biochar obtained the maximum adsorption capacity Q_m of 14.48 $mg.g^{-1}$, higher than the control BC-GCB biochar that pyrolysised without bioactive compound extraction, i.e. with Q_m of 5.41 $mg.g^{-1}$.

Keywords: Biochar, coffee waste, bioactive compound, surface area, maximum NH_4^+ adsorption

Classification numbers: 3.3.2, 3.4.2, 3.7.3.

1. INTRODUCTION

In Viet Nam, groundwater provides approximately 40 % of urban water supply and nearly 80 % of rural water supply [1]. However, the water quality of wells in Ha Nam province has shown elevated ammonium levels (2.5 - 25 $mg.L^{-1}$), exceeding permissible standards. The utilization of spent coffee grounds for biochar production offers an environmentally friendly and economical solution for groundwater ammonium treatment, capitalizing on the abundance of coffee waste generated from the thriving coffee industry in Viet Nam [2, 3]. Biochar from coffee husk impregnated with 2 M KOH as an ammonium adsorbent in water has shown high NH_4^+ adsorption capacity (Q_{max} = 51.52 mg.g^{-1}) [2], but the production used a lot of chemicals. Kizito *et al.* evaluated wood biochar and rice husk biochar in adsorbing ammonium from anaerobic pig manure sludge, with adsorption efficiency up to 60 % [4]. Do Khac Uan *et al.* have studied the use of coffee husks to produce biochar and tested ammonium removal in wastewater with high adsorption capacity (2.8 mg N.g^{-1} after 6 hours) [3]. Coffee is a main industrial crop of Viet Nam, with 2021 - 2022 exporting 1.5 million tons of Robusta coffee and generating a turnover of 2.97 billion USD. From the production, a large amount of waste coffee beans are discarded, corresponding to 50 % of the coffee consumed [5]. In recent years, there has been a trend in increasing the production of bioactive compounds such as caffeine, chlorogenic acid, or coffee extracts that serve the purpose of pharmaceutical chemistry, bringing high value to the coffee industry. The use of spent coffee grounds for making biochar to treat ammonium in groundwater would bring added value in terms of the economy and the environment.

2. MATERIALS AND METHODS

2.1. Materials

Green coffee bean was collected from Cư M'gar- Dak Lak province (Viet Nam). Ethanol 70^o of food grade was of Ha Noi Alcohol Factory (Lo Duc street, Hai Ba Trung district, Viet Nam).

2.2. Methods

Extraction of bioactive compounds from green coffee beans ground: The bean was grounded and impregnated with 70^o ethanol at the rate of 3 mL.g^{-1} for one week, then the green coffee bean extract was drained and washed, and the solid waste was dried until constant weight.

Making biochar of post-extraction coffee bean: Tightly packed 3 g of waste into a cup with a lid and carried out slow pyrolysis under anaerobic conditions with a heating rate of 1 ^{o}C.min^{-1} until 400 ^{o}C reached and stored for 30 minutes to get AC-GCB biochar.

Making biochar of green coffee beans ground without extraction: The sample pyrolysis for the green coffee ground without extraction of bioactive substances to get BC-GCB biochar. Measurement of structural parameters of AC-GCB and BC-GCB biochars.

Setting up experiments: The influence of contacting time (1.5 - 180 minutes) on the treatment efficiency was carried out at the initial NH_4^+ concentration of 25 mg.L^{-1}, pH of 6.7; biochar dose of 10 g.L^{-1}, agitation of 120 rpm. The effect of pH 1 - 9 on ammonium removal efficiency was carried out at an initial NH_4^+ concentration of 25 mg.L^{-1}, biochar dose of 10 g.L^{-1}, and agitation of 120 rpm for 90 minutes. The influence of the biochar dose (0.5; 1.0; 1.5; 2.5; 3.5; 5; 7.5; 10.0; 12.5; 15.0; 17.5 g.L^{-1}) on the ammonium removal capacity was carried out at an initial NH_4^+ concentration of 25 mg.L^{-1}, pH 6.7, agitation of 120 rpm for 90 minutes. The influence of initial NH_4^+ concentration on treatment efficiency was carried out at pH 6.7, biochar dose was 10 g.L^{-1}, agitation of 120 rpm for 90 minutes. pH was measured before and after the reaction. pH of the solution was adjusted to a given value by 0.01 M HCl and 0.01 M NaOH solutions.

Analytical methods**:** The surface area (BET) of the biochar was determined by a Surface Area Analyzer (Quantachrome Instruments, Florida, USA). The biochar microstructure was analyzed by scanning electron microscope (SEM) technique, the distribution image of NH_4^+ ions on the biochar surface was taken by Energy dispersive spectrometry (EDS) - mapping method, using JEOL- JSM6400 (Japan). The Fourier-transform infrared spectroscopy (FTIR) was done by Bruker Tensor 27 IR (USA) in spectral range from 400 cm^{-1} to 4000 cm^{-1}. The NH_4^+ concentration was determined by manual spectrometric method TCVN 6179-1:1996, ISO 7150-1:1984 at 655 nm [6].

2.3. Adsorption isotherm and kinetic model

The NH_4^+ adsorption isotherm of CGB was evaluated by Langmuir (1) and Freundlich (2) models [7].

$$\frac{C_e}{Q_e} = \frac{1}{Q_m} C_e + \frac{1}{bQ_m} \tag{1}$$

$$q_e = K_F C_e^{\frac{1}{n}} \tag{2}$$

where: q_e ($mg.g^{-1}$) and C_e ($mg.l^{-1}$) are equilibrium ammonium ion concentrations in solid phase and liquid phase, respectively; Q_m ($mg.g^{-1}$) is the maximum adsorption capacity of the material and b ($kl.g^{-1}$) is the equilibrium constant related to the adsorption energy; K_F and n are Freundlich constants. The adsorption rate is either first-order (3), or second-order (4), dependent on the capacity of the adsorbent [8]

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303} t \tag{3}$$

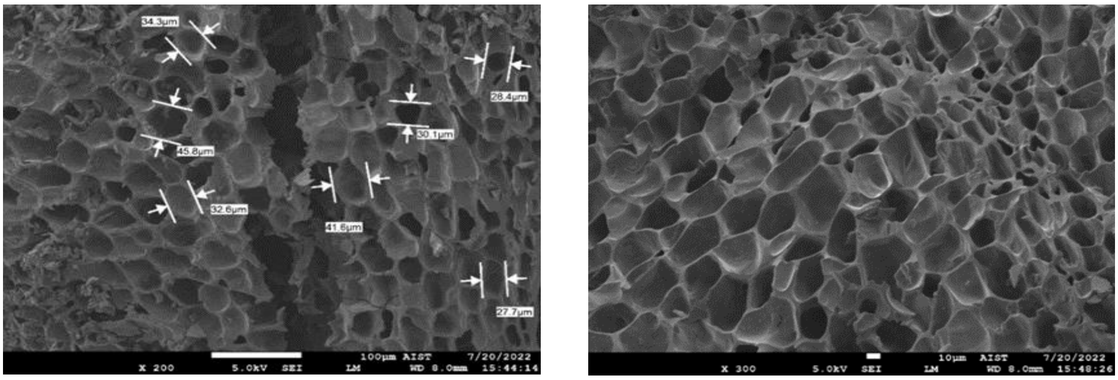
$$\frac{1}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}(t) \tag{4}$$

where: Q_t ($mg.g^{-1}$) is adsorption capacity at time t (min), Q_e ($mg.g^{-1}$) is adsorption capacity at equilibrium time, k_1 (min^{-1}) and k_2 ($g.mg^{-1}.min^{-1}$) are rate constants.

3. RESULTS AND DISCUSSION

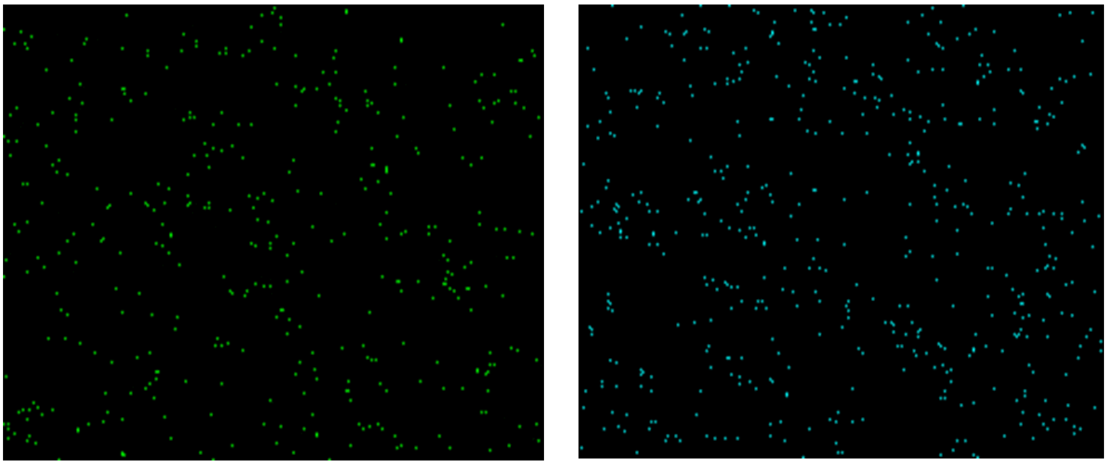
3.1. Characteristics of biochar of post-extraction coffee bean

The surface area (BET) and capillary volume of BC-GCB and AC-GCB were 0.8753 $m^2.g^{-1}$, 0.002631 $cm^3.g^{-1}$; 1.4428 $m^2.g^{-1}$, 0.003674 $cm^3.g^{-1}$, correspondingly. The SEM imaging presented in Figure 1 shows that the material has a rough surface, many pores with pore size in the range of 27 µm to 50 µm. This feature contributes to the material's good adsorption and retention capacity for pollutants. The EDS- mapping results in Figure 2 show that the biochar contains mainly C, O, K, P, N, and NH_4^+ distributed relatively uniformly on the surface of the materials. NH_4^+ density is denser in AC-GCB biochar. The FTIR spectra (Figure 3) showed that the functional groups on the surface of the biochars are in the range of 500 - 4000 cm^{-1}. The wide spectral band in the range of 3500 - 3000 cm^{-1} of both biochar due to the OH group being stretched and the OH group present in cellulose, lignin, water or can also correspond to the N-H valence oscillation in the amine (first-order and second-order) and carbohydrate groups in macromolecular compounds; the spectral band near the 1500 cm^{-1} value indicates that the C=C bond is stretched in the structure of both biochars; the band in the range of 1300 - 1000 cm^{-1} shows the appearance of C-O bond; the band at 700 cm^{-1} indicates the aromatic rings of lignin, hemicellulose and cellulose in both BC-GCB and AC-GCB materials [9]. These functional groups contribute significantly to NH_4^+ adsorption.



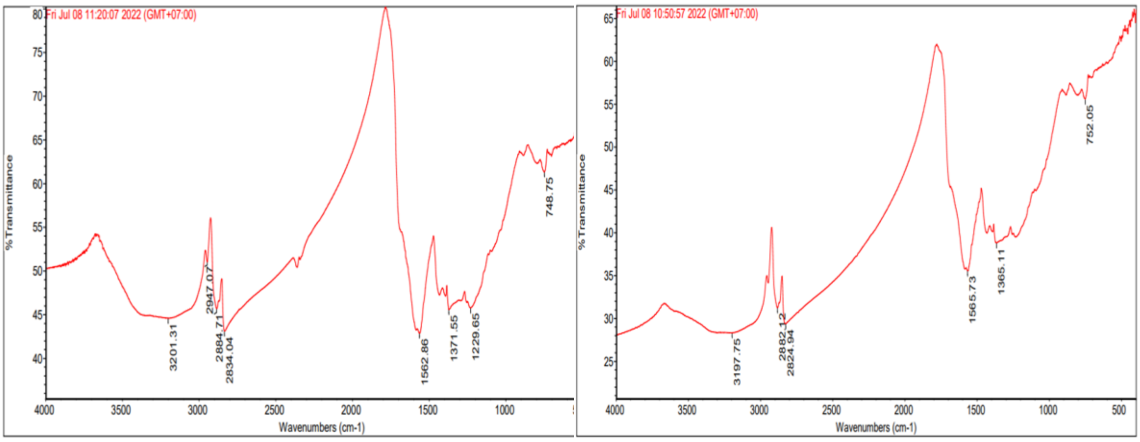
(a) (b)

Figure 1. SEM images of BC- GCB (a) and AC- GCB (b).



(a) (b)

Figure 2. EDS- mapping of distribution of NH_4^+ on the surface of BC-GCB (a) and AC- GCB (b).



(a) (b)

Figure 3. FTIR spectra of BC-GCB (a) and AC-GCB (b).

3.2 Effect of contacting time on the adsorption capacity

The effect of contacting time on ammonium treatment efficiency was carried out in the time from 2.5 to 180 min at initial pH 6.7. The Figure 4 resulted that after the first 2.5 minutes, the adsorption rate increased rapidly, reached efficiency of 46.4 % and 64.4 % in BC-GCB and AC-GCB, respectively. Between 2.5 and 10 min, the adsorption rate continued to increase, then gradually stabilized and reached equilibrium after 90 min in both BC-GCB and AC-GCB, with the treatment efficiency reaching 59.4 % and 77.6 %. This trend could be explained as follows: the initial rapid adsorption is due to the NH_4^+ replacing the positive ion on the material's surface. In the first time of contact, the biochar has a lot of vacant adsorption sites, the ammonium concentration in the water is the highest, so the adsorption process is high and leads to a rapid increase in the process efficiency. The next slower rising phase represents physical adsorption deterioration with ionic equilibrium. The slow increase is due to chemisorption and diffusion of ammonium ions inside the material, then reaches saturation of the active sites [9].

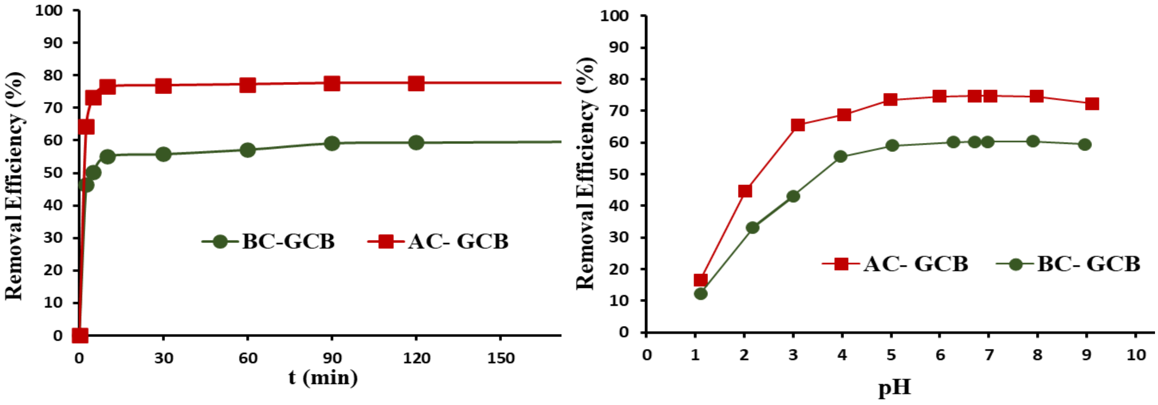


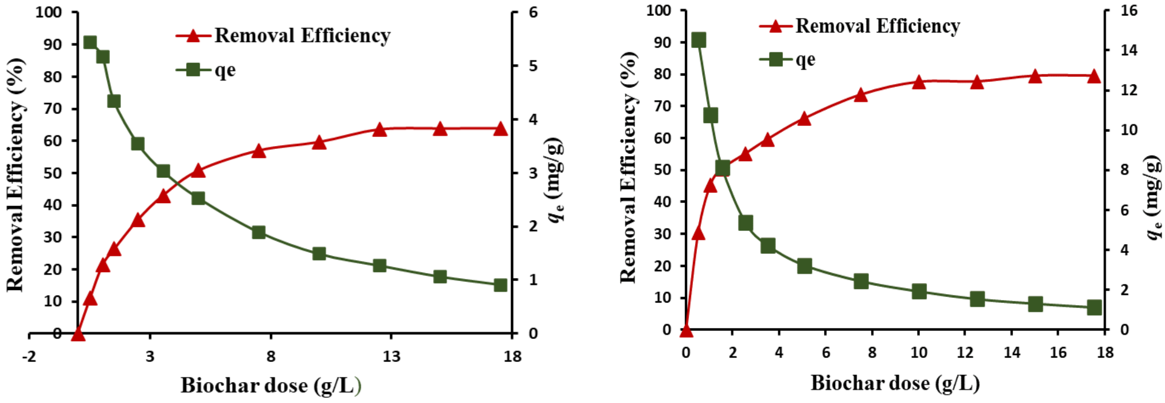
Figure 4. Influenctial factors such as (a) contact time and (b) initial pH on ammonium removal efficiency by BC-GCB and AC-GCB.

3.3 Effect of pH on the adsorption capacity

The experiment was carried out at the initial pH in the range of 1 to 9. The results in Figure 4 showed that both materials had less efficient ammonium removal at pH 1 - 2 . When the pH increased from 2 - 4, the treatment efficiency increased rapidly (from about 30 % to 60 % for BC-GCB, from 40 % to more than 70 % for AC-GCB). In the pH range from 4 to 8, the efficiency of ammonium treatment increased slowly and stabilized at about 60.3 % and 74.6 % for BC-GCB and AC-GCB, respectively. At low pH values, the ammonium adsorption capacity was lower due to the competition between H^+ and NH_4^+. When pH was increased, the adsorption efficiency increased gradually at first and then tended to decrease gradually when the pH exceeded 9. In the lower pH 6, ammonium exists as NH_4^+ ion, resulting in low adsorption efficiency [10]. As pH increased from 6 to 8, ammonium existed in the form of NH_4^+, with less competition, and the ability to bind NH_4^+ to the material's surface increased. Conversely, at high pH values, ammonium converts to the neutral form of NH_3, which also reduces the adsorption capacity. This trend was also found in previous studies [3]. An initial pH range of 6 to 8 is suggested for cost-effective treatment, as it aligns with typical groundwater pH and ensures relatively high ammonium removal efficiency.

3.4 Effect of dose of biochar on the adsorption capacity

The biochar dosage (g.L^{-1}) was carried out at pH 6.7, contact time was 90 min, there was a change in the ratio between the mass of the material and the volume of the solution in the range from 0.5 to 17.5 g.L^{-1}. Figure 5 showed that the ammonium adsorption efficiency increased rapidly from 11.1 % to 26.3 % for BC-GCB and from 30.4 % to 50.4 % for AC-GCB when the biochar dosage was in the range from 0.5 to 1.5 g.L^{-1} and gradually stabilized with increasing dose from 1.5 to 7.5 g.L^{-1}. For BC-GCB, when the biochar dosage increased to 12.5 g.L^{-1}, the treatment efficiency did not increase too much. For AC-GCB, the biochar dosage for the highest adsorption efficiency is 10 g.L^{-1}. When the material dosage is higher, the contact surface will be larger and more ammonium will be adsorbed on the surface [11]. However, when the biochar dosage was increased to a certain value, the NH_4^+ adsorption was not significantly increased because the overlap of adsorbent layers could obscure the active sites [12]. This same trend was also found in previous studies [3, 6].



(a)

(b)

Figure 5. Effect of biochar dosage on ammonium removal efficiency and amount of ammonium adsorbed on the surface of materials (a) BC-GCB and (b) AC-GCB.

3.5 Effect of initial ammonium concentration on the adsorption capacity

To investigate the influence of initial ammonium concentration, experiments were carried out with BC-GCB and AC-GCB materials at biochar dosage of 10 g.L^{-1}, agitation of 120 rpm for 90 min.The initial NH_4^+ concentration was investigated ranging from 5 to 50 mg.L^{-1}. Figure 6 showed that the initial ammonium concentration was 5 mg.L^{-1}, the treatment efficiencies of BC-GCB and AC-GCB were 73.8 % and 89.2 %, respectively. With an increase in initial ammonium concentration from 5 to 50 mg.L^{-1}, the efficiency decreased from 73.8 % to 47.9 % with BC-GCB and from 89.2 % to 62 % with AC-GCB. This reduction can be attributed to the limited maximum adsorption capacity of the materials [13]. When the material surface does not have enough adsorbent sites to adsorb ammonium, increasing the concentration of ammonium solution while keeping the same dose of material will cause the amount of free ammonium to increase while the adsorbed ammonium remains unchanged, leading to the adsorption efficiency was gradually reduced. Similar findings have been reported in previous studies [4, 14, 15].

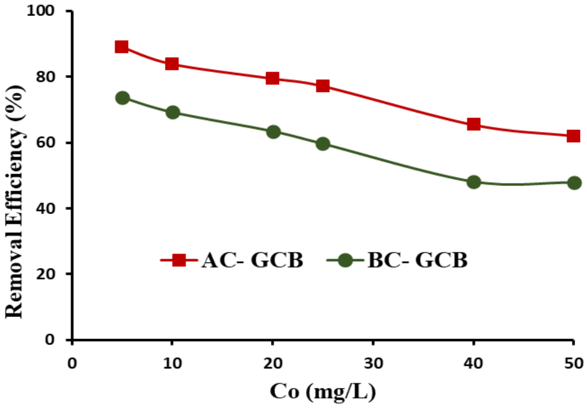


Figure 6. Effect of initial ammonium concentration on ammonium adsorption efficiency by BC-GCB and AC-GCB.

Ammonium adsorption isotherm: The studies of equilibrium in adsorption indicate the biochar adsorption capacity by Langmuir and Freundlich models that have been widely used. The experimental results are shown in Figures 7 and 8, and the constants are shown in Table 1. The suitability between the model and experimental data is shown by the correlation coefficient R^2. The correlation coefficient R^2 in Table 1 showed that NH_4^+ treatment with biochar is consistent with both Freundlich and Langmuir adsorption theory in AC-GCB (R^2 of 0.982 and 0.918). For BC-GCB, the treatment process is more consistent with Freudlich adsorption theory (R^2 of 0.963). It could be seen that the adsorption of biochar can not only describe the linear or saturation region and the working concentration range. The NH_4^+ adsorbant follows both monolayer and multilayer mechanisms. The treatment process can follow not only adsorption mechanism but also many other mechanisms (ion exchange, chemisorption, complexation...). The maximum adsorption capacity Q_m of BC-GCB biochar is 5.41 $mg.g^{-1}$, and that of AC-GCB is 14.48 $mg.g^{-1}$.

Table 1. Parameters of Langmuir and Freundlich isotherms and coefficient of determination (R^2) for model fits.

	Parameter values		R^2	
	BC- GCB	**AC- GCB**	**BC- GCB**	**AC- GCB**
Langmuir parameters			0.836	0.918
b ($L.mg^{-1}$)	0.022	0.018		
Q_m ($mg.g^{-1}$)	5.41	14.48		
Freundlich parameters			0.963	0.982
K ($mg.g^{-1}$)	0.026	0.049		
n	0.57	0.50		

***Ammonium adsorption kinetic*:** Results have been shown in Table 2 and Figures 9 and 10. However, pseudo-second order gives the value of q_e close to the experiment. It can be concluded that the NH_4^+ treatment is consistent with the pseudo-second order kinetic model.

Table 2. Kinetic models applied and parameters and coefficient of determinations (R^2) obtained from the model fits.

Parameters			R^2	
	BC- GCB	**AC- GCB**	**BC- GCB**	**AC- GCB**
Pseudo-frst order			0.934	0.773
k_1 $(1.min^{-1})$	0.038	0.040		
q_{e1} $(mg.g^{-1})$	0.45	0.24		
Pseudo-second order			0.999	1
k_2 $(g.(mg.min)^{-1})$	0.624	1.758		
q_{e2} $(mg.g^{-1})$	1.49	1.94		

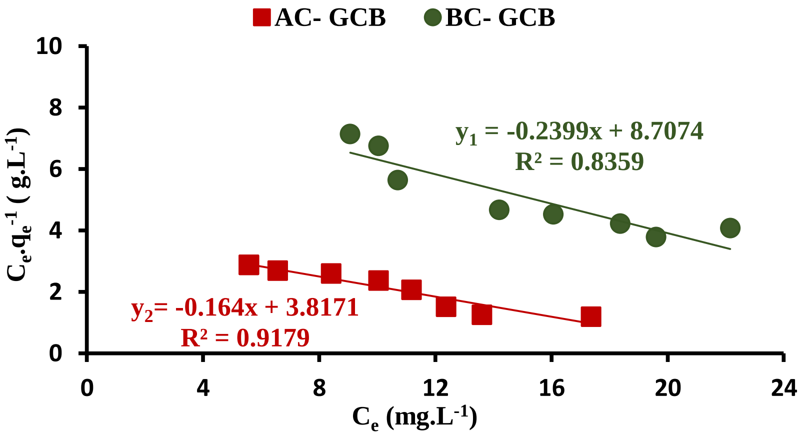


Figure 7. Langmuir model.

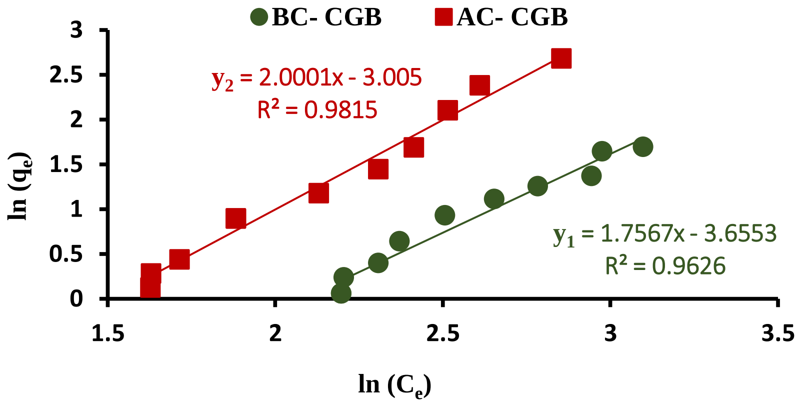


Figure 8. Freundlich model.

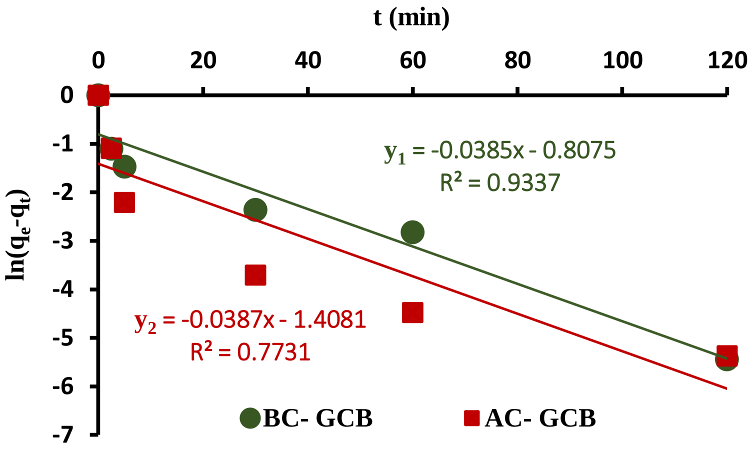


Figure 9. Pseudo-first-order model predictionof the kinetics of ammonium removal.

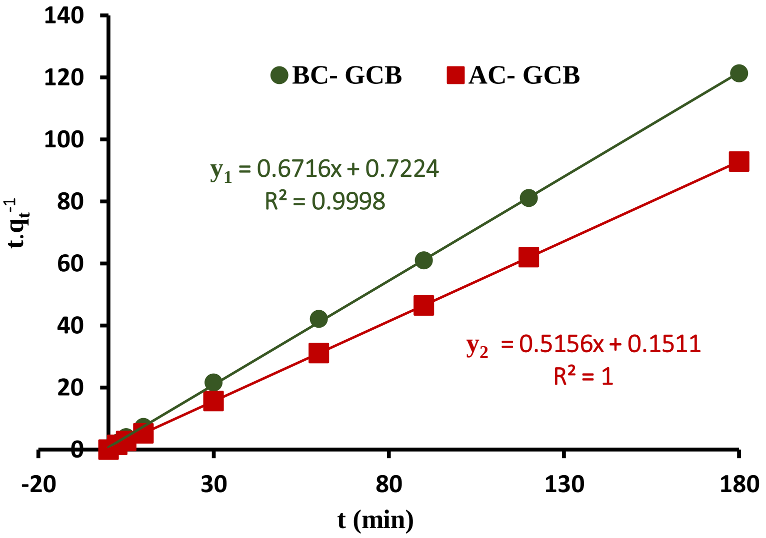


Figure 10. Pseudo-second-order model prediction of the kinetics of ammonium removal.

4. CONCLUSION

In this study, we investigated the adsorption potential of biochar of post-extraction coffee bean ground (AC-GCB) at 400 °C for ammonium removal. AC-GCB exhibited a rough surface and abundant pores with sizes ranging from 27 µm to 50 µm. During ammonium adsorption, NH_4^+ ions were uniformly and densely distributed on the AC-GCB surface due to its higher surface area of 1.4428 $m^2.g^{-1}$ compared to the control sample (BC-GCB) without bioactive compound extraction, with a surface area of 0.8753 $m^2.g^{-1}$. At 27 °C, AC-GCB biochar was suitable for pH initial range from 4 to 8, the time to equilibrium is 90 minutes, the optimal solid/liquid ratio was 10 $g.L^{-1}$, the input ammonium concentration less than 25 $mg.L^{-1}$, the ammonium removal efficiency was 77.6 %. The ammonium adsorption of AC-GCB biochar was consistent with both Langmuir and Freundlich adsorption theories with high correlation coefficients R^2 (> 0.92). Significantly, AC-GCB exhibited a higher maximum adsorption capacity (Q_m = 14.48 mg.g^{-1}) compared to the control BC-GCB biochar (Q_m = 5.41 mg.g^{-1}), which was pyrolyzed without bioactive compound extraction. The effectiveness of AC-GCB biochar as an efficient and environmentally friendly adsorbent for ammonium removal from water sources. The utilization of post-extraction coffee bean ground for biochar production offers a sustainable approach to address ammonium pollution while adding value to the coffee industry's by-products.

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CRediT authorship contribution statement. Nguyen Hoai Linh: Methodology, Investigation, Formal Analysis, Writing –original draft, Writing –review and editing. Ngo Kim Chi: Conceptualization, Funding acquisition, Project administration, Writing –review and editing. Tran Le Minh: Methodology, Writing –original draft. Dang Ngoc Phuong: Supervision. Nguyen Xuan Tung: Formal Analysis. Do Thuy Tien: Methodology, Investigation. Pham Thi Hong Minh: Supervision.

Declaration of competing interest. We declare that we have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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