CHEESA: Chemical Engineering Research Articles
ISSN 2614-8757 (Print), ISSN 2615-2347 (Online)
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Research Article

Isotherm and Kinetics Adsorption of Ammonium using Cocopeat Biochar Activated

Isoterm dan Kinetika Adsorpsi Ion Amonium menggunakan Biochar Berbahan Dasar Cocopeat Teraktivasi

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Article History
Submitted: 09th June 2025; Revised: 29th September 2025; Accepted: 11th October 2025; Available online: 11th November 2025; Published Regularly: June 2025

doi: 10.25273/cheesa.v8i1.22466.43-54

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Abstract

Nitrogen recovery from wastewater is capable of preventing eutrophication, offering economic benefits, and reducing carbon footprint from synthetic fertilizer production. Biochar has been explored as adsorbent for ammonium (NH_4^+) removal. Therefore, this study aimed to investigate the potential of biochar derived from cocopeat as adsorbent for NH_4^+ removal. Cocopeat was modified by potassium hydroxide (KOH) and pyrolyzed at 500°C for 2 h to produce activated biochar. Kinetics and isotherm studies were conducted to examine adsorption mechanisms. Fourier Transform Infrared (FTIR) data showed that the resulting biochar after activation and adsorption contained hydroxyl O–H and C–O groups, while a new N–H band confirmed the interaction with NH_4^+ ions. Biochar adsorbed NH_4^+ ions with a maximum capacity of 0.3078 mg/g. FTIR spectra showed shifts and changes in the intensity of functional group bands, confirming the interaction between NH_4^+ ion and the active sites on biochar surface. Adsorption followed Langmuir isotherm and pseudo-first-order kinetics model, with an optimal contact time of 5 h. These results suggested that cocopeat-based biochar had potential as an effective NH_4^+ adsorbent.

Keywords: adsorption kinetics; ammonium removal; cocopeat biochar; potassium hydroxide

Abstrak

Pemulihan nitrogen dari air limbah dapat mencegah eutrofikasi, memberikan manfaat ekonomi, dan mengurangi jejak karbon dari produksi pupuk sintetis. Biochar telah dieksplorasi sebagai adsorben untuk menghilangkan amonium. Penelitian ini bertujuan untuk mengkaji potensi biochar yang berasal dari cocopeat sebagai adsorben untuk menghilangkan ion ammonium. Cocopeat yang telah dimodifikasi dengan KOH selanjutnya dilakukan pirolisis pada suhu 500 °C selama 2 jam untuk memperoleh biochar teraktivasi. Modifikasi karbon dengan KOH bertujuan untuk meningkatkan porositas dan luas permukaan karbon aktif. Data FTIR menunjukkan bahwa biochar yang dihasilkan setelah aktivasi dan adsorpsi masih memiliki gugus hidroksil (O–H) dan C–O, sedangkan munculnya pita baru N–H mengonfirmasi terjadinya interaksi biochar dengan ion amonium. Penelitian ini menunjukkan bahwa biochar dapat mengadsorpsi ion amonium (NH_4^+) dengan kapasitas maksimum sebesar 0,3078 mg/g. Analisis FTIR mengindikasikan adanya interaksi antara biochar dan ion amonium melalui gugus fungsi tersebut. Proses adsorpsi dan kinetika mengikuti model Langmuir dan pseudo orde pertama dengan waktu kontak optimum selama 5 jam. Biochar ini berpotensi digunakan sebagai adsorben ion ammonium.

***Kata kunci**: adsorpsi amonium; cocopeat biochar; kinetika adsorpsi; KOH*

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1. Introduction

High concentrations of ammonium (NH_4^+) in wastewater is a factor that leads to eutrophication and oxygen depletion in aquatic environments [1]. Various treatment technologies have been developed to remove NH_4^+ from water, including physical (membrane filtration, ion exchange, adsorption), chemical (precipitation, oxidation), and biological processes (photobioreactors, membrane bioreactors) [2],[3]. Chemical methods show high effectiveness, membranes are associated with high operational costs, while biological methods are more economical but typically slower. Membrane-based physical methods require high investment and technical expertise. In correspondence with the increasing interest on circular economy and valuable waste recovery [4], adsorption using renewable adsorbent materials is considered a simple, efficient, and feasible method. According to Lee et al. [5], carbon-based materials such as biochar, activated carbon have attracted significant attention for NH_4^+ removal.

Biochar produced from biomass is widely regarded as a low-cost, accessible, and environmentally sustainable technology [6]. Among various biomass sources, plant-based waste is preferred [5]. Coconut represents a highly versatile agricultural commodity with broad potential for waste valorisation. Despite the broad cultivation and economic value, several parts of the coconut tree, such as coconut coir, remain insufficiently used. This lignocellulosic waste can be transformed into value-added products such as cocopeat blocks to enhance agricultural productivity, or further processed into biochar, offering a sustainable solution with both economic and ecological benefits [7].

The carbon-rich material, known as biochar, which is produced through pyrolysis of biomass under limited oxygen conditions, has gained attention for the environmental benefits and sorption capabilities. The high specific surface area, pore volume, oxygen-containing functional groups, and cation exchange capacity make it particularly effective for removing NH_4^+ through physical adsorption and electrostatic interactions. As reported by Anisuzzaman et al. [8], activation using potassium hydroxide (KOH) enhances the porosity and surface area of biochar by intercalating potassium into the carbon matrix, generating well-developed micropores and mesopores suitable for NH_4^+ adsorption. Cocopeat-derived biochar activated with KOH is studied for NH_4^+ adsorption capacity through adsorption isotherm, kinetics, and material characterization analyses. Functional groups such as carboxyl (-COOH), hydroxyl (-OH), and carbonyl (C=O) contribute to NH_4^+ binding through electrostatic interactions and ion exchange [9], while the alkaline nature of the material can raise soil pH, enhancing nutrient stability and availability. Post-adsorption, biochar serves as a slow-release fertilizer, improving soil quality and nutrient retention [10].

Previous studies by Warsidah et al. [11], He et al. [12], and Xiao et al. [13] have explored a wide range of biomass such as sugarcane bagasse, corn stalks, and wheat straw. Various modification methods have been used to enhance adsorption performance. Vu et al. [14] found that corn cob biochar treated with HNO_3 and NaOH showed a maximum NH_4^+ adsorption capacity of 22.6 mg/g

Munar-Florez et al. [15] reported the achievement of 1.49 mg/g by K_2CO_3-modified palm shell biochar. An et al. [16] found that KOH-modified peanut shell

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biochar adsorbed approximately 6.92 mg/g of NH_4^+. Wang et al. [17] reported $LaCl_3$-modified sawdust biochar to have reached 10.1 mg/g. Despite showing limited NH_4^+ adsorption, potassium–iron modified rice straw biochar contributes to improved soil fertility [18] due to the presence of potassium, a macronutrient essential for plant growth that plays a key role in nutrient uptake and soil productivity. Investigations on KOH-activated cocopeat biochar as NH_4^+ adsorbent remain limited. Therefore, this study aimed to investigate the physicochemical characteristics of KOH-activated cocopeat biochar and evaluate NH_4^+ adsorption capacity through isotherm and kinetics studies.

2. Research Methods

2.1. Materials

In this study, cocopeat supplied by CV. Sumbersari, Ledokombo District, Jember was used as the raw material. The experimental materials comprised ammonium chloride (NH_4Cl, Pudak), distilled water (aquadest), hydrochloric acid (HCl, 32%), KOH (Pudak), phenol (89%, Sigma-Aldrich), ethyl alcohol (95%), sodium nitroprusside (Merck), trisodium citrate (Pudak), sodium hydroxide (NaOH, Pudak), and sodium hypochlorite (NaClO, 5%, Pudak).

2.2. Tools

The experimental tools included a furnace for pyrolysis at 500°C, a pH meter (Kalstein) to monitor solution pH during adsorption process, a UV–Vis spectrophotometer (Shimadzu UV-1780) to determine the concentration of NH_4^+ based on absorbance at 640 nm, and Fourier Transform Infrared (FTIR) spectrophotometer (Thermo scientific Nicolet iS-10) to identify functional groups present on biochar surface before and after NH_4^+ adsorption. The spectra were measured in transmittance mode in the range 4000–500 cm^{-1}, and the powdered biochar samples were thoroughly mixed with potassium bromide (KBr) powder.

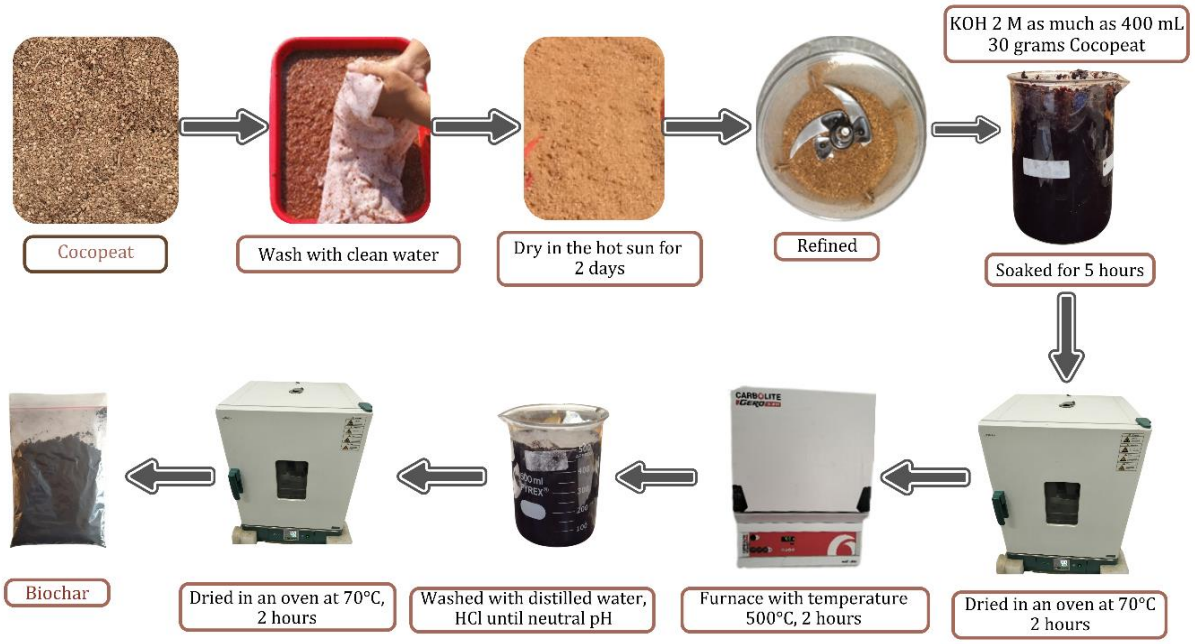

Figure 1. Biochar synthesis scheme from cocopeat

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2.3. Methods

2.3.1. Pretreatment of Cocopeat

Raw cocopeat (3 kg) was washed twice with running water to remove dust and impurities, then filtered using a cloth. The washed material was sun-dried for two days, producing approximately 1.5 kg of dried cocopeat, which corresponded to a ~50% reduction in moisture content. The dried cocopeat was sieved through a 60-mesh screen to obtain uniform particles, and 150 g of the sieved material was stored for further use.

2.3.2. Cocopeat Activation

Cocopeat of 30 g was impregnated with 400 mL of 2 M KOH solution. The mixture was stirred and soaked for 5 h in a covered glass beaker to minimize evaporation. The pre-treated cocopeat was oven-dried at 70°C for 2 h, followed by pyrolysis in a muffle furnace at 500°C for 2 h. The resulting black biochar was washed with distilled water and diluted hydrochloric acid (HCl) until neutral pH was achieved, and subsequently dried at 70°C. The dried form was stored in a desiccator prior to characterization and adsorption experiments. The process of biochar synthesis from cocopeat is presented in Figure 1.

2.3.3. Adsorption Experiments

The effect of initial NH_4^+ ion concentration on adsorption capacity was evaluated at 0.1–0.5 mg/L using 2 g/L of biochar at pH 7. The assesment of adsorption kinetics was carried out by performing experiments at 0.4 mg/L NH_4^+ for contact times ranging from 1 to 6 h under identical conditions. Specifically, adsorption capacity (q_e) was calculated based on the difference between initial and equilibrium NH_4^+ concentrations.

NH_4^+ concentration was measured following Indonesian National Standard (SNI 06-6989.30-2005). A 10 mL aliquot of each sample was reacted with 0.4 mL phenol, 0.4 mL sodium nitroprusside, and 1 mL oxidizing reagent, then mixed thoroughly, covered with aluminum foil, and allowed to develop color for 1 h. Absorbance was measured at 640 nm using a UV-Vis spectrophotometer.

2.3.4. Adsorption Isotherm

Adsorption isotherm was assessed by mixing 0.2 g of biochar with 100 mL of NH_4^+ solution (0.1–0.5 mg/L). The mixture was shaken at 120 rpm for 5 h and filtered, then the residual NH_4^+ concentration was analyzed using the method described above.

Isotherm models were applied to evaluate adsorption mechanism. Freundlich model is presented in equation (1) and the linear form in equation (2) [19], while equation (3) shows Langmuir model. q_e represents adsorption capacity (mg/g), K_F is Freundlich constant, C_e implies equilibrium concentration (mg/L), 1/n signifies adsorption intensity [20], K_L is Langmuir constant (L/mg), and q_{max} is maximum adsorption capacity (mg/g) [21]. The isotherm model fitting was evaluated using linear regression (R^2), with values closer to 1 suggesting a better fit [22].

$$q_e = K_F C_e^{\frac{1}{n}} \quad \text{.....(1)}$$

$$\log qe = \log K_F + \frac{1}{n}\log Ce \quad \text{.....(2)}$$

$$\frac{1}{qe} = \left(\frac{1}{q_{max}K_L}\right) \times \left(\frac{1}{C_e}\right) + \frac{1}{q_{max}} \quad \text{.....(3)}$$

2.3.5. Adsorption Kinetics

Kinetics studies were conducted at 0.4 mg/L NH_4^+ for varying contact times (1–6 h). Adsorption capacity at time (q_t) was measured and fitted to two kinetics models.

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Pseudo first order and pseudo second order are presented in equations (4) and (5) [23].

$$\log(q_e - q_t) = \log qe - \frac{k_1}{2{,}303}t \quad \text{.....(4)}$$

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

q_t = Adsorption capacity at time (mg/g).
q_e = Adsorption capacity at equilibrium (mg/g).
k_1, k_2 = rate constants.
t = time

3. Results and Discussion

3.1 Fourier Transform Infrared (FTIR)

FTIR analysis was conducted to identify the functional groups present in KOH-activated cocopeat biochar. Figure 2 presents FTIR spectra of raw cocopeat, KOH-activated biochar prior to adsorption, and KOH-activated biochar after NH_4^+ ion adsorption. Table 1 shows a summary of the functional groups identified from these spectra.

FTIR spectra of raw cocopeat show prominent peaks at 3442 cm^{-1} (O-H stretching) [24], 2926 cm^{-1} (C-H *stretching*) [1], 1741 cm^{-1} (C=O *stretching*), 1633 cm^{-1} (C=C *stretching*) [25], 1429 cm^{-1} (O-H *bending*), and 1058 cm^{-1} (C-O *stretching*) [1]. After carbonization, FTIR spectra of biochar still show similar peaks at 3417 cm^{-1} (O-H *stretching*) [24], 2927 cm^{-1} (C-H *stretching*) [1], 1627 cm^{-1} (C=C *stretching*) [25], 1408 cm^{-1} (O-H *bending*), and 1070 cm^{-1} (C-O *stretching*) [1]. However, the intensities of these peaks decrease, signifying a weakening of the chemical structure due to the removal of volatile compounds during the pyrolysis process.

Following NH_4^+ adsorption, FTIR spectra of biochar show a further weakened O–H stretching peak at 3410 cm^{-1}, suggesting the participation of hydroxyl groups in electrostatic interactions with NH_4^+ [26]. C=C stretching peak at 1616 cm^{-1} remains relatively unchanged [25], and a new peak appears at 1558 cm^{-1}, corresponding to N–H bending, which signifies the successful adsorption of NH_4^+ on biochar surface [3]. The peaks at 1408 cm^{-1} (O-H *bending*) [1] and 1068 cm^{-1} (C-O stretching) are present, suggesting that functional groups containing oxygen (O–H and C–O) remain intact post-adsorption [1].

The observed spectral changes confirm the occurrence of chemical interactions between NH_4^+ and the functional groups on biochar surface, primarily through electrostatic attraction. The shift of O–H stretching peak from 3442 cm^{-1} to 3410 cm^{-1} signifies interaction between hydroxyl groups and NH_4^+. Additionally, the formation of N–H bending peak at 1558 cm^{-1} supports the presence of adsorbed NH_4^+ ions, possibly replacing potassium ions (K^+) at the active sites.

Table 1. FTIR absorption bands of raw cocopeat and modified cocopeat biochar

Number of Waves (cm^{-1})				
Raw Cocopeat	Activated Biochar (before adsorption)	Activated Biochar (after NH_4^+ adsorption)	Peak Analysis	Ref
3442	3417	3410	O-H stretching	[24]
2926	2927	-	C-H stretching	[1]
1741	-	-	C=O stretching	[25]
1633	1627	1616	C=C stretching	[25]
-	-	1558	N-H bending	[3]
1429	1408	1408	O-H bending	[1]
1058	1070	1068	C-O stretching	[1]

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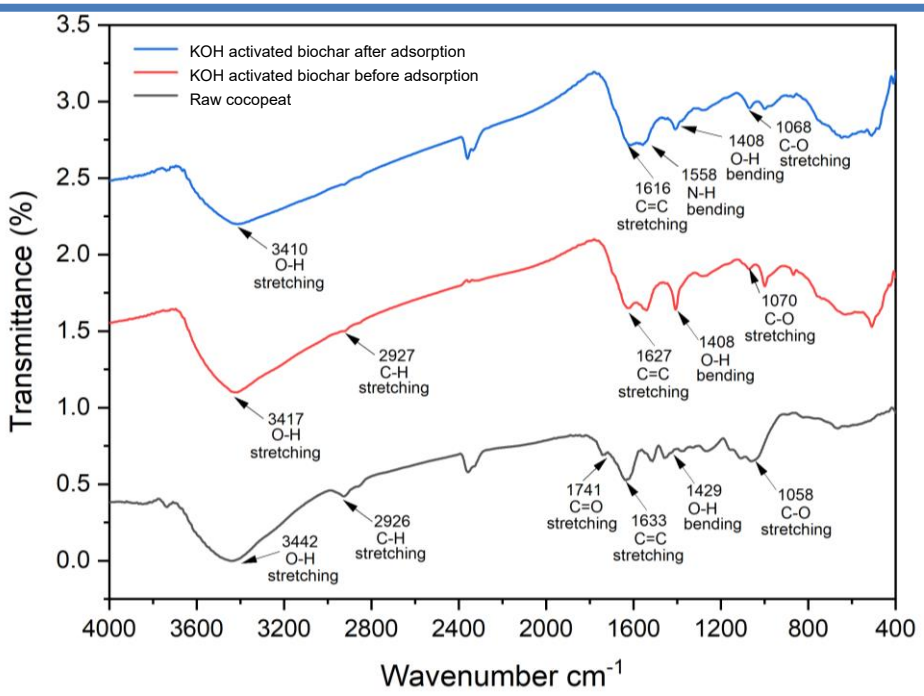

Figure 2. FTIR spectra of raw cocopeat, KOH-activated biochar before and after NH_4^+ adsorption

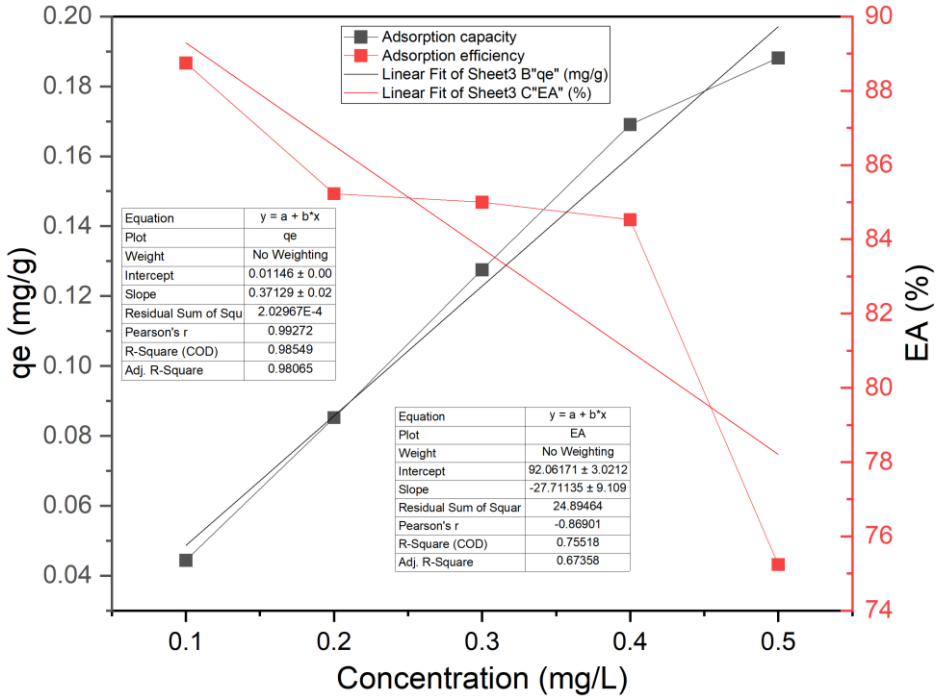

Figure 3. Adsorption capacity and removal efficiency of KOH-activated biochar

3.2 Adsorption Isotherm

The standard curve was constructed by measuring the absorbance of a series of NH_4^+ standard solutions with known concentrations using a UV–Vis spectrophotometer. The linear regression equation of standard curve was y = 0.7109x + 0.021, with a determination coefficient (R^2) of 0.9902. Adsorption capacity refers to the equilibrium uptake of NH_4^+ by KOH-activated cocopeat biochar [20]. According to Figure 3, adsorption capacity increases with the initial NH_4^+ concentration, implying that the availability of NH_4^+ in

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solution significantly influences the occupation of active sites on biochar surface. This process occurs primarily through electrostatic interactions between positively charged NH_4^+ and negatively charged functional groups such as carbonyl (C=O), hydroxyl (–OH), and carboxyl (–COOH) present on biochar surface [27].

Figure 3 shows adsorption efficiency, which reflects the ability of biochar to remove NH_4^+ from solutions with varying initial concentrations [28]. The efficiency is highest at low NH_4^+ concentrations and decreases as the concentration increases. This observation can be attributed to the limited number of active sites on biochar. At higher concentrations, the active sites become saturated, reducing the total adsorption efficiency. Additionally, the high adsorption efficiency at lower concentrations suggests that KOH activation successfully enhances the pore structure and introduces functional groups facilitating effective NH_4^+ adsorption [1].

Langmuir and Freundlich isotherm models were used to understand adsorption mechanism. Langmuir isotherm describes monolayer adsorption on homogeneous surfaces [29]. Based on Langmuir isotherm data shown in Figure 4, Langmuir constants (q_m and K_L) were calculated, as presented in Table 2. The activated biochar has a considerable adsorption capacity of 0.3078 mg/g toward NH_4^+. The high R^2 value supports the applicability of Langmuir model, implying that adsorption process occurs as monolayer coverage where each adsorption site accommodates a single NH_4^+.

Freundlich isotherm accounts for multilayer adsorption on heterogeneous surfaces. As shown in Freundlich isotherm plot (Figure 4), Freundlich constant (K_F) reflects adsorption capacity at low concentrations, while the exponent value (1/n) represents adsorption intensity. The positive value of n (1.5573) indicates favorable adsorption, suggesting that NH_4^+ ions are effectively adsorbed onto the surface of activated cocopeat biochar. Moreover, comparing the R^2 values of Langmuir and Freundlich models helps determine the most suitable isotherm model to represent adsorption behavior of the activated biochar. In this study, Langmuir model provided a better fit, suggesting that adsorption mechanism primarily follows a monolayer process.

Based on the analysis of adsorption isotherms, KOH-activated cocopeat biochar has good performance in NH_4^+ adsorption. The dominant adsorption behavior follows Langmuir model, as presented in Table 2, showing monolayer adsorption on a relatively homogeneous surface. However, the contribution of multilayer adsorption, as described by Freundlich model, plays a minor role, particularly on the heterogeneous regions of biochar surface.

Table 2. Adsorption isothermal parameters of NH_4^+ removal with activated cocopeat biochar

Isotherm	Parameters		
Freundlich	Intercept	:	-0.0715
	Slope	:	0.6421
	n	:	1.5573
	K_f	:	0.8481
	R^2	:	0.9300
Langmuir	Intercept	:	3.2484
	Slope	:	0.2193
	q_{max} (mg/g)	:	0.3078
	K_L	:	14.8111
	R_L	:	0.1190
	R^2	:	0.9861

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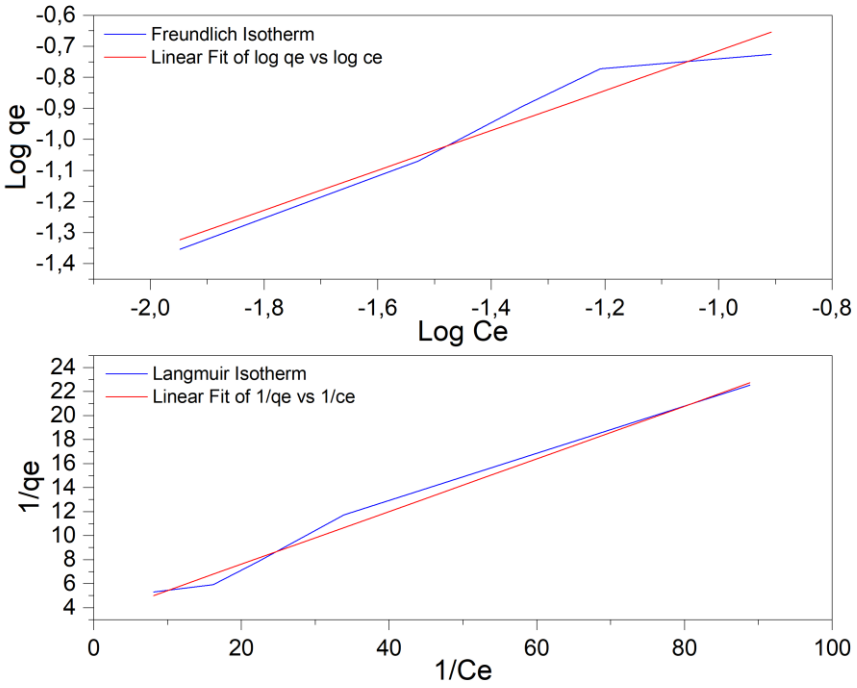

Figure 4. Isotherm adsorption curve of NH_4^+ removal with activated cocopeat biochar**:** Freundlich isotherm (top) and Langmuir isotherm (bottom)

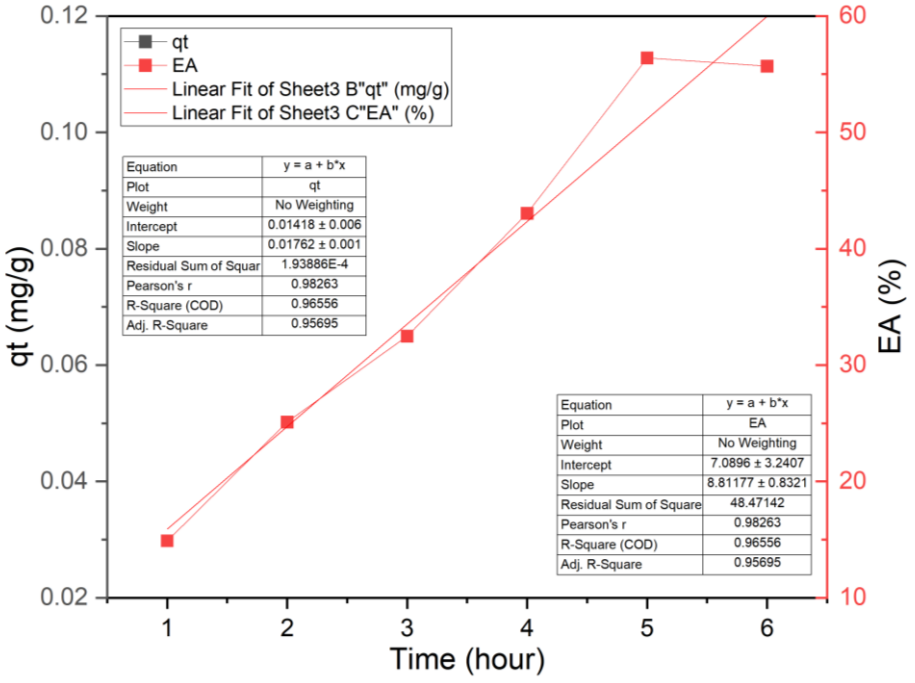

Figure 5. Adsorption capacity of NH_4^+ removal with activated cocopeat biochar as a function of contact time (C_0 = 0,4 mg/L)

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3.3 Adsorption Kinetics

Based on the data presented in Figure 5, adsorption capacity of NH_4^+ by KOH-activated biochar increases with contact time from 1 to 5 h but decreases at 6 h, representing a shift in adsorption behavior. Initially, adsorption capacity (q_t) was approximately 0.030 mg/g, which increased to 0.113 mg/g at the fifth hour. This trend suggests that prolonged contact time facilitates greater interaction between NH_4^+ and the active sites of biochar, promoting the approach toward adsorption equilibrium. However, the decline observed at 6 h implies that excessive contact time may lead to desorption of the previously adsorbed ions or the system has reached saturation [30]. The results show that the optimal contact time for NH_4^+ adsorption is 5 h, defined as the duration required to establish equilibrium between adsorbed and residual solute concentrations in the system [31].

Adsorption efficiency presented a consistent increase up to 5 h, where efficiency was around 15% at the initial stage, rising to 56% after 5 h. This improvement reflects enhanced utilization of adsorbent surface over time. However, a decrease in efficiency was observed at the 6-h mark, corresponding to potential saturation or desorption phenomena. Similar behavior has been reported in previous studies, where NH_4^+ removal using coffee ground-based biochar reached equilibrium at approximately 40 minutes, beyond which no significant improvement was observed due to saturation of active sites [1].

Comparable results were observed in biochar derived from coconut coir, where adsorption capacity followed a similar increasing trend. This consistency across different biochar sources shows the effectiveness as adsorbents for NH_4^+ removal from aqueous solutions. The results confirm that KOH-activated biochar is a promising material for NH_4^+ adsorption, although the efficiency of the process may decline beyond the optimal contact duration.

Pseudo-first-order and pseudo-second-order kinetics models were applied to analyze adsorption mechanism of NH_4^+ onto KOH-activated coconut coir biochar. These models differ in the underlying assumptions and implications. Pseudo-first-order model assumes that the rate of adsorption is proportional to the number of unoccupied sites and primarily associated with physisorption processes including weak van der Waals interactions or diffusion control. However, pseudo-second-order model presumes that chemisorption is the rate-limiting step, including electron sharing or exchange between adsorbent and adsorbate. The suitability of each model was evaluated based on the determination coefficient (R^2) as well as the consistency between the calculated and experimental adsorption capacities (q_e). Kinetics model provides insights into the rate-limiting steps and optimal contact time for adsorption process [31].

Table 3. Adsorption kinetics study parameter of NH_4^+ removal with activated cocopeat biochar

Kinetics Models	$q_{e,cal}$ (mg/g)	Constant		R^2
		value	unit	
Pseudo first order	0.1750	0.197	min^{-1}	0.937
Pseudo second order	0.3036	0.334	min^{-1}	0.762

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As shown in Table 3, NH_4^+ adsorption process is better described by pseudo-first-order kinetics model. This conclusion is supported by the calculated adsorption capacity ($q_{e,cal}$) of 0.1750 mg/g, which is very close to the experimental adsorption capacity of 0.169 mg/g obtained from the initial concentration 0.4 mg/L in isotherm study (Figure 3). The high R^2 value of 0.937 further supports the appropriateness of the model, signifying that 93.7% of the data variation can be explained by pseudo-first-order model.

Pseudo-second-order model produced a $q_{e,cal}$ value of 0.3036 mg/g that significantly exceeded the experimental value and generated a lower R^2 of 0.762. This suggests that pseudo-second-order model does not accurately represent the kinetics behavior of NH_4^+ adsorption by biochar under the studied conditions.

Pseudo-first order-model, with a rate constant of 0.197 min^{-1}, is considered more suitable for describing NH_4^+ adsorption process onto activated biochar. Kinetics data were analyzed using both pseudo first order and pseudo second order models to determine adsorption mechanism of NH_4^+ onto KOH-activated cocopeat biochar. Pseudo-first-order model produced a calculated equilibrium adsorption capacity ($q_{e,cal}$) of 0.1750 mg/g, which is very close to the experimental value (0.1691 mg/g), with a high correlation coefficient (R^2 = 0.937). Meanwhile, pseudo-second-order model produced a significantly higher $q_{e,cal}$ of 0.3036 mg/g, which deviated from the experimental result and had a lower R^2 value (0.762).

The results suggest that NH_4^+ adsorption process more closely follows pseudo-first-order model, implying that the rate-limiting step is probably governed by diffusion-controlled mechanisms. Although pseudo-second-order model is often associated with chemisorption processes including electron sharing or exchange, the observed poor fit shows that the mechanisms are not dominant in this system. Pseudo-first-order model better represents kinetics behavior of NH_4^+ adsorption onto KOH-activated cocopeat biochar under the tested conditions. Further evaluation is required, but the presence of retained NH_4^+ in biochar suggests the potential as a nitrogen-enriched soil amendment.

4. Conclusion

In conclusion, KOH-activated cocopeat biochar showed effective adsorption performance for NH_4^+ ions (NH_4^+) in aqueous solutions. FTIR analysis confirmed interactions between NH_4^+ and surface functional group, evidenced by a weakened O–H stretching band and the formation of a new peak at 1558 cm^{-1} (N–H bending). Adsorption data fitted well with Langmuir isotherm model, suggesting monolayer adsorption on a homogeneous surface, which had a maximum theoretical adsorption capacity of 0.3078 mg/g. Kinetics studies followed pseudo-first-order model, suggesting that diffusion-controlled mechanisms might dominate. Adsorption efficiency increased with contact time up to 5 h, after which it declined due to the saturation of active sites or partial desorption.

Acknowledgments

The authors are grateful for the support and funding provided by the Internal Research Grant of LP2M Universitas Jember, in collaboration with CV Sumbersari, which facilitated the execution of this study project.

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