

Research Article

Calcium Ion Adsorption-Desorption Behavior on Maize Residue-Derived Biochar for Soil Nutrient Retention

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ABSTRACT

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This research investigated the adsorption and desorption behavior of calcium ion (Ca^{2+}) on maize residue-derived biochar prepared by pyrolysis at 400 °C for 3 h under oxygen-limited conditions. Batch adsorption experiments were conducted by mixing 1.0 g biochar with 30 mL Ca^{2+} solutions at initial concentrations of 50-90 mg/L and shaking at 100 rpm until equilibrium. The produced biochar had an alkaline pH of 8.11, a specific surface area of 22.51 m²/g, a pore volume of 0.04 cm³/g, and oxygen-containing functional groups including -OH, -COOH/C=O, C-O, and phenolic groups. Adsorption equilibrium was reached after 240 min. The adsorption data fitted the Freundlich model ($R^2 = 0.9828$; KF = 1.6792 L/g; $1/n = 1.6567$) better than the Langmuir model ($R^2 = 0.8478$), while negative Langmuir parameters indicated that the monolayer assumption was not appropriate for this system. Kinetic analysis showed better agreement with the pseudo-second-order model ($R^2 = 1.00$; q_e , cal = 1.170 mg/g), suggesting that surface complexation or ion-exchange interactions contributed to the first adsorption layer. Subsequent retention might involve weaker adsorbate-adsorbate interactions on heterogeneous sites, consistent with Freundlich-type multilayer adsorption. The hysteresis index (HI = 1.37) suggested relatively strong calcium retention with limited desorption in deionized water. These findings indicate that maize residue-derived biochar has potential as a calcium-retention soil amendment; however, soil incubation and plant-response studies are required to validate agricultural performance under practical conditions.

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1. Introduction

Maize productivity in Thailand has gradually declined over the past decade, largely due to soil degradation caused by intensive monoculture, excessive fertilizer application, and post-harvest residue burning (Office of Agricultural Economics, 2023; Aumtong *et al.*, 2024). These practices reduce soil organic matter, deteriorate soil structure, and decrease cation exchange capacity (CEC), thereby weakening the soil's ability to retain exchangeable nutrient cations and accelerating nutrient losses through leaching (Khongdee *et al.*, 2022; Omara *et al.*, 2023). Among essential plant nutrients, calcium (Ca^{2+}) is particularly susceptible to leaching in acidic and highly weathered soils despite its indispensable roles in cell wall stabilization, membrane integrity, intracellular signaling, and plant tolerance

to biotic and abiotic stresses (Wdowiak *et al.*, 2024). Consequently, improving calcium retention while maintaining its availability has become an important challenge for sustainable agricultural production.

Calcium is an essential secondary macronutrient that regulates numerous physiological processes, including enzyme activation, root development, and cellular signaling, in addition to its structural role in plant cell walls (Wdowiak *et al.*, 2024). However, because Ca^{2+} is relatively weakly retained by soil colloids compared with many other nutrient cations, it is readily lost through leaching, particularly in coarse-textured and acidic soils. Therefore, effective soil amendments should not only enhance calcium retention but also allow its gradual release to satisfy plant nutrient demand throughout the growing season (Omara *et al.*, 2023). This requirement has stimulated growing

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interest in developing sustainable soil amendments capable of improving nutrient retention without restricting nutrient availability.

Among the available soil amendments, biochar has emerged as a promising material because of its porous structure, large specific surface area, high cation exchange capacity, and abundant oxygen-containing functional groups generated during oxygen-limited pyrolysis (Amalina *et al.*, 2022; Phadtare and Kalbande, 2022; Kabir *et al.*, 2023). These physicochemical properties promote nutrient retention through cation exchange, electrostatic attraction, and surface complexation while simultaneously improving soil physical properties (Kabir *et al.*, 2023; Omara *et al.*, 2023). Nevertheless, high adsorption capacity alone does not necessarily ensure improved nutrient use efficiency if adsorbed nutrients cannot subsequently be released for plant uptake. Therefore, comprehensive evaluation of both adsorption and desorption behavior is essential for assessing the practical agricultural performance of biochar. In this context, hysteresis analysis provides valuable information on nutrient retention and release behavior beyond conventional adsorption capacity.

Existing studies have demonstrated that biochar effectively adsorbs various metal cations owing to its porous structure and oxygen-containing functional groups (Chen *et al.*, 2024; Mei *et al.*, 2025). However, most investigations have focused on the removal of heavy metals and other environmental contaminants rather than nutrient cations such as Ca^{2+} . Moreover, previous studies have primarily emphasized adsorption equilibrium, while calcium desorption behavior, hysteresis characteristics, and the relationships among adsorption isotherms, adsorption kinetics, and nutrient release remain insufficiently understood. Consequently, it remains unclear whether calcium adsorbed onto biochar can be retained strongly enough to minimize nutrient loss while still being gradually released to satisfy plant nutrient requirements, particularly in maize residue-derived biochar.

Maize residues are among the most abundant agricultural by-products generated annually in northern Thailand and are frequently disposed of by open-field burning, resulting in greenhouse gas emissions and the loss of valuable biomass resources. Compared with many agricultural residues, maize residues are inexpensive, locally available, and produced in large quantities, making them an attractive feedstock for biochar production. Furthermore, biochar produced from maize residues under relatively low pyrolysis temperatures has been reported to preserve abundant oxygen-containing functional groups that favor nutrient cation adsorption (Janu *et al.*, 2022; Barszcz *et al.*, 2024). Low-temperature pyrolysis (approximately 400 °C) preserves these reactive functional groups while maintaining adequate pore development, whereas higher pyrolysis temperatures promote aromatic carbon formation and reduce

surface oxygen functionalities involved in cation adsorption (Janu *et al.*, 2022; Barszcz *et al.*, 2024).

Based on these considerations, this study aims to characterize the physicochemical properties of maize residue-derived biochar and systematically investigate calcium absorption, adsorption kinetics, desorption behavior, and hysteresis characteristics. Unlike previous studies that mainly evaluated adsorption equilibrium of contaminant metals, this work integrates physicochemical characterization, adsorption isotherm analysis, kinetic modeling, desorption experiments, and hysteresis evaluation to provide a comprehensive understanding of calcium retention and release mechanisms on maize residue-derived biochar. The findings are expected to provide a more realistic assessment of biochar performance as a sustainable nutrient-retention material capable of simultaneously minimizing calcium loss through leaching while maintaining adequate nutrient availability for plant uptake.

2. Materials and Methods

2.1 Maize residue preparation

The maize residue used for biochar production was collected from local farmers in the Jedee Maekrua community, Mae Faek Mai, San Sai, Chiang Mai, Thailand. The collected maize residues were sun-dried for 7 days to remove moisture. After drying, the residues were mechanically ground at a rotational speed of 14,000 rounds per minute (rpm) for 3 minutes. The ground material was then sieved through a 60-mesh screen to obtain fine maize residue powder. This powder was stored in a desiccator to prevent moisture absorption before further use.

2.2 Conversion of maize residue into biochar

The maize residue powder, previously sieved through a 60-mesh screen, was converted into biochar by using a pyrolysis process. The pyrolysis process was conducted under oxygen-limited conditions at a temperature of 400 °C, with a heating rate of 5 °C per minute, for a duration of 3 hours. This process yielded fine black biochar powder. The fine black biochar powder was subsequently sieved again using a 60-mesh screen to ensure uniform particle size. The biochar powder was then stored in a desiccator to prevent moisture absorption prior to use.

2.3 Chemical composition and physical property analysis of biochar

The chemical composition analysis of biochar was performed to identify and confirm the presence of functional groups on the biochar surface, such as hydroxyl (–OH), carboxyl (–COOH), and carbonyl (C=O) groups. This was carried out using a Fourier Transform Infrared Spectrometer (FTIR) (Perkin Elmer, England/Spectrum) over a wavenumber range of 400–4000 cm^{-1} . The chemical properties of the biochar were further assessed by measuring pH using a pH meter (Mettler-Toledo AG) and cation exchange capacity (CEC) following the method described by Intanoo and Kongklay (2022). For physical characterization, the specific surface area, pore size, and pore

volume of the biochar were analyzed using a surface area and porosity analyzer based on the Brunauer–Emmett–Teller (BET) method (Quantachrome/Autosorb 1 MP).

2.4 The adsorption and release behavior of calcium ions on the surface of biochar

The adsorption behavior of calcium ions on the biochar surface was studied based on adsorption equilibrium theories using the Langmuir model (Equations (1)–(2)) (Langmuir, 1918) and the Freundlich model (Equations (3)–(4)) (Freundlich, 1906). Both models describe the relationship between the amount of adsorbate (calcium ions) adsorbed per unit mass of adsorbent (biochar) in mg/g, and the equilibrium concentration of calcium ions remaining in the solution at a given temperature in mg/L. The adsorption and release behavior was conducted in two stages: (1) the determination of equilibrium sorption time, and (2) the analysis of calcium ion adsorption behavior. Calcium concentrations were quantified using atomic absorption spectrophotometry (GBC Scientific Equipment/ SavantAA) following calibration with a five-point standard curve (0–100 mg/L). The calibration curve exhibited $R^2 > 0.999$.

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (1)$$

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \quad (2)$$

$$q_e = K_F C_e^{\frac{1}{n}} \quad (3)$$

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (4)$$

$$HI = \frac{1/n_{desorbed}}{1/n_{adsorped}} \quad (5)$$

where: q_e is the amount of adsorbate adsorbed per unit mass of adsorbent at equilibrium (g/g); C_e is the equilibrium concentration of the adsorbate remaining in the solution at a given temperature (g/mL); q_m is the maximum adsorption capacity for monolayer coverage per unit mass of adsorbent (g/g); K_L is the Langmuir constant related to the affinity of binding sites (L/mg); K_F is the Freundlich constant indicating the multilayer adsorption capacity (g/g).

2.4.1 Equilibrium sorption time determination

The determination of equilibrium sorption time of calcium ions onto the biochar surface was carried out by adding 30 mL of a calcium standard solution at a certain concentration to 1 gram of biochar. The mixture was then shaken at the speed of 100 rounds per minute (rpm) for various durations time: 4, 10, 15, 30, 60, 120, 240, 360, 480, and 900 minutes, respectively. After each specified shaking time, the samples were collected, and the solution was separated by filtration through a 0.45-micron nylon membrane filter. The calcium

concentration in the filtrate was determined as described in Section 2.4. All equilibrium adsorption experiments were independently performed in five replicates ($n = 5$).

2.4.2 Calcium ion adsorption behavior

The study of calcium ion adsorption behavior on the biochar surface was conducted by introducing 30 mL of calcium standard solutions with the concentrations of 50, 60, 70, 80, and 90 mg/L into 1 gram of biochar. The selected calcium concentration range of 50–90 mg/L was chosen as a controlled laboratory range suitable for evaluating adsorption isotherm behavior without causing immediate saturation of adsorption sites. This range also provided sufficient analytical sensitivity for calcium determination by atomic absorption spectrophotometry while allowing adsorption behavior to be compared across increasing initial calcium concentrations. The solution volume-to-biochar ratio of 30 mL/g was used to ensure adequate contact between calcium ions and the biochar surface under batch adsorption conditions. (Udawatta *et al.*, 2023). The mixtures were agitated using a shaker at a speed of 100 rpm for a duration corresponding to the previously determined equilibrium sorption time. A blank control containing calcium solution without biochar was simultaneously prepared under identical experimental conditions to distinguish calcium adsorption from possible precipitation during the adsorption experiment. After shaking, the solution was collected and filtered through a 0.45-micron nylon membrane filter. The calcium concentration in the filtrate was determined as described in Section 2.4. All adsorption experiments were independently performed in five replicates ($n = 5$).

2.4.3 The release of calcium ion from biochar surface

The release behavior of calcium ions (Ca^{2+}) from biochar surface was investigated using the hysteresis index (HI) as an indicator to assess the ease or difficulty of calcium ion desorption after adsorption onto biochar (Guedes *et al.*, 2021). The hysteresis index is calculated as the ratio of the slope of the adsorption curve to that of the desorption curve at the same equilibrium concentration, as shown in Equation (5). In this study, the calcium-loaded biochar (obtained from the adsorption procedure described in section 2.4.2) was immersed in 30 mL of deionized water and agitated at 100 rpm using a shaker at the equilibrium sorption time. The aqueous solution was then collected and filtered through a 0.45-micron nylon membrane filter. The concentration of desorbed calcium ions was analyzed using an atomic absorption spectrophotometer (GBC Scientific Equipment/SavantAA).

2.5 Statistical analysis

Experimental results are presented as mean $\pm$ standard deviation (SD). The mean and standard deviation were calculated from five independent experiments using Microsoft Excel 2021. Adsorption isotherm and kinetic parameters were estimated by linear regression analysis.

3. Results and Discussion

3.1 Properties of biochar

The produced biochar exhibited a cation exchange capacity (CEC) of $1,670.96 \pm 44.66$ cmol/kg and a pH of 8.12 ± 0.22 , representing approximately 38.0-fold and 1.15-fold increases, respectively, compared with the untreated soil (soil CEC = 44.00 ± 1.50 cmol/kg). These properties indicated a high density of exchangeable surface sites together with moderately alkaline characteristics that were favorable for nutrient retention. In addition, the produced biochar exhibited a specific surface area of 22.51 m²/g and a pore volume of 0.04 cm³/g, suggesting a porous structure that can facilitate interactions between nutrient ions and the biochar surface.

The relatively high CEC observed in the present study might be attributed to the preservation of oxygen-containing functional groups and the presence of mineral ash generated during low-temperature pyrolysis, both of which contribute to the formation of negatively charged adsorption sites for nutrient cations (Kabir *et al.*, 2023; Omara *et al.*, 2023; Chen *et al.*, 2024). Previous studies had similarly reported that biochars produced at relatively low pyrolysis temperatures (300–500 °C) generally exhibit higher CEC because oxygen-containing functional groups were better preserved than those produced at higher temperatures, thereby enhancing cation exchange capacity (Ippolito *et al.*, 2020; Joseph *et al.*, 2021).

The high CEC observed in this study is consistent with the potential of biochar to improve soil nutrient retention. For example, Intanoo and Kongklay (2022) reported that incorporating biochar into soil increased soil CEC by 10.33% compared with untreated soil and was associated with improved chlorophyll content and higher yields of kale and eggplant. Although the present study did not include soil incubation or plant growth experiments, the high CEC and porous structure of the produced maize residue-derived biochar suggest its potential as a nutrient-retention material for agricultural soils. Further soil and plant studies are required to verify its agronomic performance under field conditions.

The FTIR analysis of produced biochar is shown in Figure 1. As seen in Figure 1, it was found that produced biochar revealed the presence of several key functional groups on its surface. These included hydroxyl groups (O–H stretching at $3,600\text{--}3,200$ cm⁻¹), carboxylic groups (C=O stretching at $1,740\text{--}1,700$ cm⁻¹), and ether groups (C–O stretching at $1,110\text{--}1,030$ cm⁻¹). Additionally, aromatic structures (C=C, C=O stretching at $1,630\text{--}1,600$ cm⁻¹) and phenolic groups (O–H bending at $1,392$ cm⁻¹) were also detected. The dominant oxygen-containing functional groups were mainly found on biochar surface. They were attributed to partial oxidation reactions during the pyrolysis of maize residue under low-temperature (400 °C) and oxygen-limited conditions. Under such conditions, organic structures like cellulose, hemicellulose, and lignin decompose and undergo

chemical transformations, leading to the development of new surface functional groups. For the porosity of biochar, it originates from the thermal decomposition of these organic structures, which generates volatile compounds such as CO, CO₂, CH₄, H₂, and water vapor. As these volatiles release, they leave behind the cavities within the carbon matrix, by which creating the porous structure that characterizes biochar. These features collectively enhance the functionality of biochar in improving soil structure, water retention, and nutrient-retaining capacity.

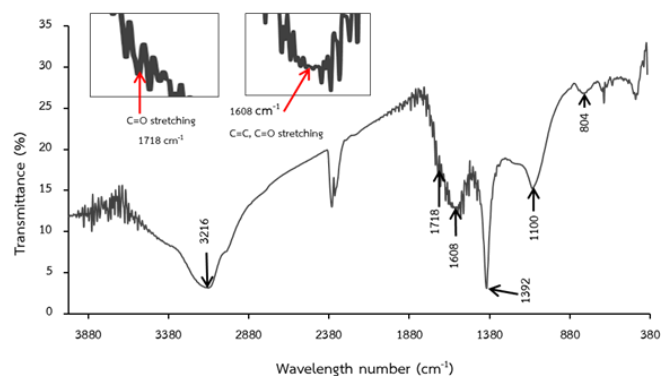


Figure 1 FTIR spectra of biochar produced from maize residue.

The presence of various functional groups on the biochar surface has attracted significant attention due to their role in enhancing the soil's cation exchange capacity (CEC). These surface functional groups, such as carboxylic (–COOH), hydroxyl (–OH), and carbonyl (C=O), can dissociate to form negatively charged sites (e.g., $R\text{--COOH} \rightarrow R\text{--COO}^-$), thereby enabling the adsorption of nutrient cations from soil solution. Therefore, the incorporating biochar into agricultural soils, might enhance the nutrient retention by reducing leaching losses, as the negatively charged sites on the biochar surface bind positively charged nutrient ions. Furthermore, elevated CEC contributes to improved fertilizer use efficiency, enriches soil fertility, and ultimately increases crop productivity.

3.2 Calcium ion adsorption behavior on the surface of biochar

3.2.1 Equilibrium sorption time determination

To determine the equilibrium sorption time of calcium ions on the biochar surface, a relationship was established between the amount of calcium adsorbed per unit mass of biochar at a given time (q_t) and the adsorption time, as illustrated in Figure 2. According to Figure 2, the amount of calcium ions adsorbed on the biochar surface increased with time and eventually stabilized after 240 minutes of adsorption. This indicates that adsorption beyond 240 minutes does not significantly affect the quantity of calcium ions adsorbed on biochar surface. In other words, once the biochar becomes saturated with calcium ions, some ions began to desorb, creating new vacant sites for subsequent ions to occupy. Eventually, the rate of adsorption equaled to the rate of

desorption, a condition known as equilibrium. This phenomenon occurred after more than 240 minutes of the adsorption. Therefore, it can be concluded that the equilibrium sorption time of this study was longer than 240 minutes.

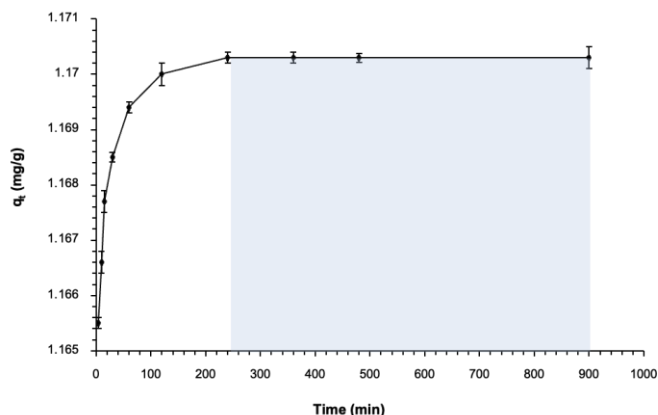


Figure 2 The adsorption of calcium ions on biochar surface at different contact times at room temperature (values represent mean $\pm$ SD ($n = 5$)).

3.2.2 Calcium ion adsorption behavior analysis

The adsorption behavior of calcium ions on the biochar surface was evaluated using the Langmuir and Freundlich adsorption isotherm models. The experimental equilibrium adsorption data obtained at initial Ca^{2+} concentrations of 50–90 mg/L are summarized in Table 1. These data were subsequently used for fitting the Langmuir and Freundlich adsorption isotherm models. The linearized Langmuir plot (Figure 3 a) yielded negative values for both the maximum adsorption capacity (q_m) and the Langmuir constant (K_L) (Table 2). Such negative parameters indicated that the fundamental assumptions of the Langmuir model, namely homogeneous adsorption sites and monolayer adsorption, were not satisfied under the present experimental conditions (Hu *et al.*, 2022; Mei *et al.*, 2025). Consequently, the Langmuir model was considered unsuitable for describing calcium adsorption onto maize residue-derived biochar, and its parameters were not interpreted quantitatively. In contrast, the Freundlich model exhibited a higher coefficient of determination ($R^2 = 0.98$) than the Langmuir model ($R^2 = 0.85$), indicating better agreement with the experimental data (Lonappan *et al.*, 2016; Khan *et al.*, 2018). This finding suggested that calcium adsorption occurred predominantly on heterogeneous adsorption sites through a multilayer adsorption process, which was consistent with the assumptions of the Freundlich isotherm.

The heterogeneous adsorption behavior might be associated with the physicochemical characteristics of the produced biochar. Biochar prepared at the relatively low pyrolysis temperature of 400 °C under oxygen-limited conditions generally retained abundant oxygen-containing functional groups while limiting the development of highly condensed aromatic structures (Janu *et al.*, 2022; Barszcz *et al.*, 2024;

Malik *et al.*, 2025). The coexistence of different functional groups likely generated adsorption sites with varying binding affinities for calcium ions, thereby promoting heterogeneous and multilayer adsorption rather than uniform monolayer adsorption. These observations were consistent with previous studies reporting that low-temperature biochars commonly exhibit heterogeneous surface characteristics that are better described by the Freundlich adsorption model (Mei *et al.*, 2025).

Based on the adsorption isotherm analysis, the Freundlich model suggested that calcium adsorption on maize residue-derived biochar occurred predominantly on heterogeneous adsorption sites through a multilayer adsorption process. As illustrated in Figure 4, the initial adsorption layer was likely associated with interactions between Ca^{2+} ions and oxygen-containing functional groups on the biochar surface, including hydroxyl and carboxyl groups. These surface interactions were generally attributed to electrostatic attraction, ion exchange, and surface complexation, which collectively contribute to relatively strong adsorption at the biochar surface (Udawatta *et al.*, 2023). Once the primary adsorption sites became occupied, additional calcium ions were likely retained through interactions with previously adsorbed ions, forming subsequent adsorption layers via relatively weak intermolecular forces, such as van der Waals and dipole–dipole interactions. This combination of strong surface interactions followed by weaker adsorbate–adsorbate interactions is consistent with the heterogeneous and multilayer adsorption behavior described by the Freundlich isotherm.

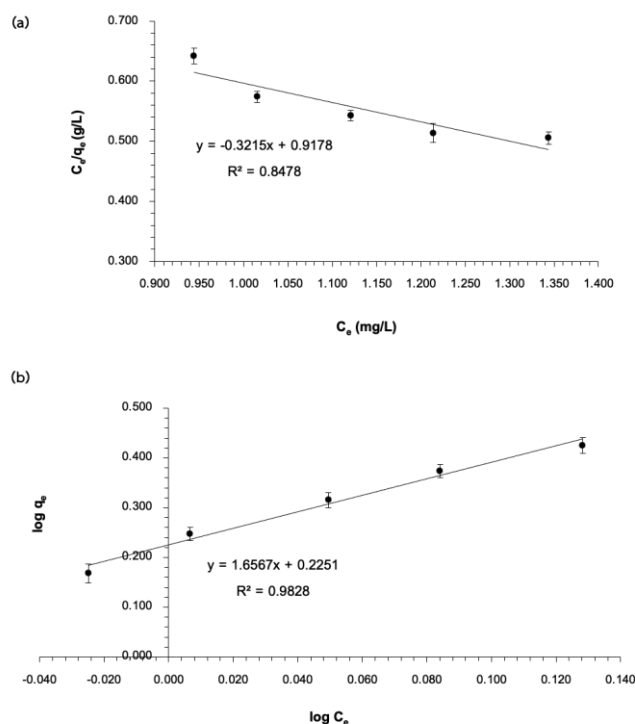


Figure 3 The adsorption behavior of calcium on biochar surface based on (a) the Langmuir and (b) the Freundlich isotherm models (values represent mean $\pm$ SD ($n = 5$)).

In the Freundlich isotherm model, the adsorption behavior was further interpreted using the constants K_F and $1/n$, which represented the adsorption capacity and adsorption intensity, respectively. The obtained $1/n$ value of 1.66 suggested that calcium adsorption deviated from ideal monolayer behavior and further supported the heterogeneous nature of the biochar surface. This observation was consistent with the superior fit of the Freundlich model and indicated that calcium adsorption likely occurred through multiple adsorption sites with different binding energies rather than uniformly distributed adsorption sites. The relatively high K_F value also reflected the favorable affinity of maize residue-derived biochar for calcium ions within the investigated concentration range. Values of $1/n$ greater than unity might indicate cooperative adsorption behavior or suggested that the Freundlich model only partially described the adsorption process over the investigated concentration range (Foo and Hameed, 2010; Tran *et al.*, 2017).

where: k_1 is the rate constant of the pseudo-first-order kinetic model (min^{-1}), q_t is the amount of adsorbate adsorbed per unit mass of adsorbent at time t (mg/g), q_e is the amount of adsorbate adsorbed per unit mass of adsorbent at equilibrium (mg/g), and t is the adsorption time (minutes).

The adsorption kinetics of calcium ions onto maize residue-derived biochar were evaluated using the pseudo-first-order and pseudo-second-order kinetic models. Linear plots generated from Equations (6) and (7) are presented in Figure 5, and the corresponding kinetic parameters are summarized in Table 3. The pseudo-second-order model exhibited a higher coefficient of determination ($R^2 = 1.00$) than the pseudo-first-order model, indicating better agreement with the experimental data. In addition, the equilibrium adsorption capacity predicted by the pseudo-second-order model ($q_{e_{cal}}$) closely matched the experimentally determined value ($q_{e_{exp}}$) of 1.170 mg/g, further supporting the suitability of this kinetic model for describing calcium adsorption onto the biochar surface.

The superior fit of the pseudo-second-order model suggested that the adsorption process was likely governed by surface interactions between calcium ions and reactive sites on the biochar rather than by simple diffusion-controlled adsorption alone. Similar kinetic behavior had been reported for calcium adsorption onto biochar and other carbonaceous adsorbents, where ion exchange and surface complexation were considered important adsorption pathways (Udawatta *et al.*, 2023). Nevertheless, the kinetic analysis alone could not conclusively identify the adsorption mechanism. Therefore, the adsorption mechanism proposed in this study was interpreted collectively based on adsorption isotherm analysis together with FTIR characterization and hysteresis behavior. Overall, these complementary results suggested that calcium adsorption on maize residue-derived biochar likely involved relatively strong surface interactions during the initial adsorption stage, followed by weaker interactions contributing to multilayer adsorption, which is consistent with the Freundlich adsorption model.

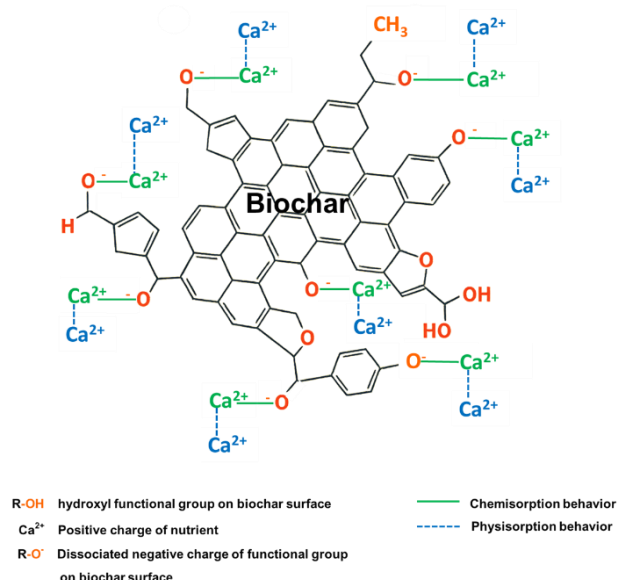


Figure 4 Schematic drawing of multilayer adsorption following the Freundlich adsorption isotherm model.

3.2.3 Adsorption kinetics

The study of calcium ion adsorption kinetics on the biochar surface provides insights into the adsorption efficiency, which might be governed either by the diffusion of calcium ions toward the biochar surface, as described by the pseudo-first-order kinetic model (Equation (6)), or by the formation of chemical bonds between calcium ions and the surface functional groups of the biochar, as explained by the pseudo-second-order kinetic model (Equation (7)) (Udawatta *et al.*, 2023).

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (6)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (7)$$

3.3 Calcium ion desorption from biochar surface

The desorption behavior of calcium ions from maize residue-derived biochar was evaluated using the hysteresis index (HI), which reflected the reversibility of the adsorption-desorption process. In general, low HI values indicated weak nutrient retention and a greater risk of nutrient loss through leaching, whereas excessively high HI values suggested that adsorbed nutrients might become strongly retained and less available for plant uptake (Guedes *et al.*, 2021). Therefore, an appropriate balance between adsorption and desorption was essential for biochar intended for agricultural applications.

In the present study, the calculated HI value was 1.37, indicating that calcium ions were retained on the biochar surface while remaining potentially releasable under appropriate environmental conditions. This result suggested that maize residue-derived biochar possesses a favorable balance

between calcium retention and release rather than exhibiting either excessively weak or irreversible adsorption. The observed hysteresis behavior was also consistent with the Freundlich isotherm, which indicated heterogeneous adsorption sites and multilayer adsorption. Calcium ions initially associated with reactive oxygen-containing functional groups may be retained more strongly, whereas ions adsorbed in subsequent layers were expected to be more readily desorbed through weaker intermolecular interactions.

Although the present study was conducted under controlled laboratory conditions, the obtained HI value suggested that the produced biochar had the potential to function as a nutrient-retention material capable of reducing calcium loss while maintaining nutrient availability. Such adsorption–desorption behavior might contribute to improved nutrient use efficiency in agricultural soils. However, the actual release of calcium under field conditions was expected to be influenced by various environmental factors, including soil pH, moisture content, competing ions, and microbial activity. Therefore, soil incubation and plant growth experiments were required to verify the practical agronomic performance of the produced biochar.

Although the present study provided insight into the adsorption and desorption behavior of calcium ions on maize residue-derived biochar under controlled laboratory conditions, several limitations should be acknowledged. The adsorption experiments were performed using standard calcium solutions rather than soil systems, and solution pH was not continuously monitored during adsorption. Consequently, the possible influence of solution chemistry on calcium precipitation cannot be completely excluded. Furthermore, the agricultural implications proposed in this study should be considered

preliminary until validated through soil incubation and plant growth experiments. Future studies should therefore investigate calcium retention under realistic soil conditions while incorporating pH monitoring and blank control experiments.

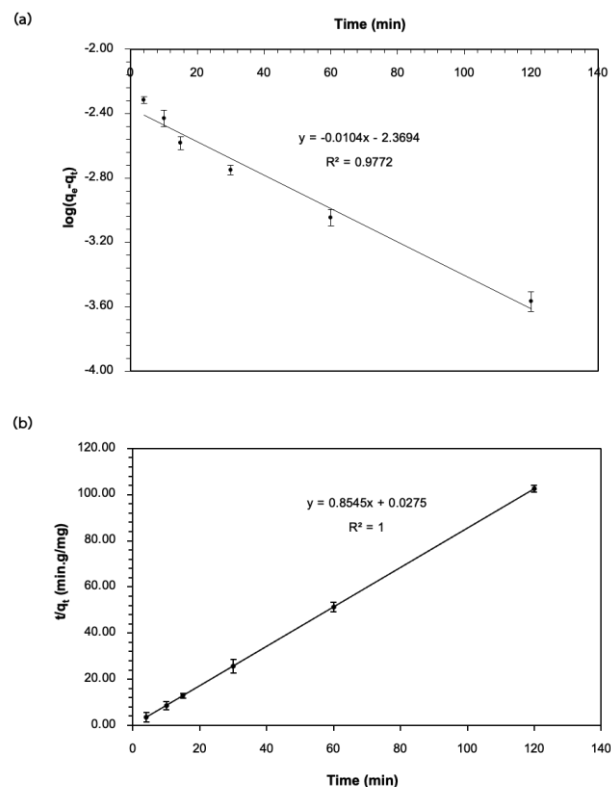


Figure 5 The adsorption kinetics of calcium ion on biochar surface based on (a) the pseudo-first-order and (b) the pseudo-second-order reaction rate (values represent mean $\pm$ SD ($n = 5$)).

Table 1 The calcium ion adsorption data on 1 gram of biochar were analyzed using the Langmuir and Freundlich isotherm model at room temperature.

Concentration (mg/l)		q_e (mg/g)	C_e (mg/l)	$\frac{C_e}{q_e}$ (g/l)	$\log C_e$	$\log q_e$
Initial	Adsorbed					
50	49.06	1.472	0.944	0.642	-0.025	0.168
60	58.98	1.770	1.015	0.574	0.007	0.248
70	68.88	2.066	1.121	0.542	0.050	0.315
80	78.79	2.364	1.214	0.513	0.084	0.374
90	88.66	2.660	1.344	0.505	0.128	0.425

Table 2 The parameters that describe the adsorption behavior according to the Langmuir and the Freundlich isotherm model.

Langmuir adsorption isotherm			Freundlich adsorption isotherm		
q_m (mg/g)	K_L (L/mg)	R^2	K_F (L/g)	$1/n$	R^2
-3.1104	-0.3503	0.8478	1.6792	1.6567	0.9828

Table 3 The kinetic constants of calcium ion adsorption on biochar based surface on the pseudo-first-order and pseudo-second-order reaction rate.

$q_{e\text{ (exp)}}^*$ (mg g^{-1})	Pseudo-first order reaction rate			Pseudo-second order reaction rate		
	$q_{e\text{ (cal)}}^{**}$	k_1	R^2	$q_{e\text{ (cal)}}^{**}$	k_2	R^2
	(mg g^{-1})	(min^{-1})		(mg g^{-1})	($\text{g mg}^{-1} \text{ min}^{-1}$)	
1.170	0.00427	0.0239	0.9772	1.170	26.56	1.00

Note: $q_{e\text{ (exp)}}^*$ is calcium absorption capacity at equilibrium obtained from the experiment.

$q_{e\text{ (cal)}}^{**}$ is calcium adsorption capacity at equilibrium obtained from the calculation.

4. Conclusion

The study of calcium ion adsorption behavior on the biochar surface revealed that the adsorption mechanism aligns with the Freundlich isotherm model. This reflects adsorption on heterogeneous surface sites of biochar and supports multilayer adsorption. The adsorption process was found to involve both chemisorption and physisorption mechanisms. In the first adsorption layer, calcium ions bind to surface functional groups containing oxygen atoms such as $-\text{OH}$, $-\text{COOH}$, and $\text{C}=\text{O}$ through chemical bonding, which corresponded to the pseudo-second-order kinetic model. In subsequent layers, additional calcium ions are adsorbed onto the initially adsorbed calcium ions through physical forces such as electrostatic interactions and van der Waals forces. These interactions further support the occurrence of multilayer adsorption, consistent with the heterogeneous nature of the biochar surface. Furthermore, desorption analysis showed that the hysteresis index (HI) was greater than 1.00, indicating the adsorbed calcium ions were strongly retained on the biochar surface. These results suggested that the produced biochar demonstrated promising calcium ion retention capability.

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6. References

Amalina, F., Razak, A.S.A., Krishnan, S., Sulaiman, H., Zularisam, A.W. and Nasrullah, M. 2022. Biochar production techniques utilizing biomass waste-derived materials and environmental applications: A review. **Journal of Hazardous Materials Advances** 7: 100134.

Barszcz, W., Łożyńska, M. and Molenda, J. 2024. Impact of pyrolysis process conditions on the structure of biochar obtained from apple waste. **Scientific Reports** 14: 10501.

Chen, J., Zhou, J., Zheng, W., Leng, S., Ai, Z., Zhang, W., Yang, Z., Yang, J., Xu, Z., Cao, J., Zhang, M., Leng, L. and Li, H. 2024. A complete review on the oxygen-containing functional groups of biochar: Formation mechanisms, detection methods, engineering, and applications. **Science of the Total Environment** 946: 174081.

Foo, K.Y. and Hameed, B.H. 2010. Insights into the modeling of adsorption isotherm systems. **Chemical Engineering Journal** 156(1): 2–10.

Freundlich, H. 1906. Over the adsorption in solution. **Zeitschrift für Physikalische Chemie** 57: 387–470.

Guedes, R.S., Pinto, D.A., Ramos, S.J., Dias, Y.N., Junior, C.F.C., Gastauer, M., Filho, W.M.S. and Fernandes, A.R. 2021. Biochar and conventional compost reduce hysteresis and increase phosphorus desorbability in iron mining waste. **Revista Brasileira de Ciência do Solo** 45: e0200174.

Hu, Y., Li, P., Yang, Y., Ling, M. and Li, X. 2022. Preparation and characterization of biochar from four types of waste biomass under matched conditions. **BioResources** 17(4): 6464–6475.

Intanoo, P. and Kongklay, K. 2022. A study of kale and eggplant growth growing in biochar-based growing media. **Journal of Agricultural Research and Extension** 40(1): 1–14.

Ippolito, J.A., Cui, L., Kammann, C., Wrage-Mönnig, N., Estavillo, J.M., Fuertes-Mendizabal, T., Novak, J.M., Spokas, K.A., Borchard, N. and Cayuela, M.L. 2020. Biochar as a sustainable strategy to improve soil properties and nutrient use efficiency: A review. **Agronomy** 10(10): 1567.

Janu, R., Mrlik, V., Ribitsch, D., Hofman, J., Sedláček, P., Bielská, L. and Soja, G. 2022. Biochar surface functional groups as affected by biomass feedstock, biochar composition and pyrolysis temperature. **Carbon Resources Conversion** 5(1): 36–46.

Joseph, S., Cowie, A.L., Van Zwieten, L., Bolan, N., Budai, A., Buss, W., Cayuela, M.L., Graber, E.R., Ippolito, J.A., Kuzyakov, Y., Luo, Y., Ok, Y.S., Palansooriya, K.N.,

- Shepherd, J., Stephens, S., Weng, Z. and Lehmann, J. 2021. How biochar works, and when it doesn't: A review of mechanisms controlling soil and plant responses to biochar. **GCB Bioenergy** 13(11): 1731–1764.
- Kabir, E., Kim, K.H. and Kwon, E.E. 2023. Biochar as a tool for the improvement of soil and environment. **Frontiers in Environmental Science** 11: 1324533.
- Khan, M.A., Khan, S., Ding, X., Khan, A. and Alam, M. 2018. The effects of biochar and rice husk on adsorption and desorption of cadmium onto soils with different water conditions (upland and saturated). **Chemosphere** 193: 1120–1126.
- Khongdee, N., Tongkoom, K., Iamsaard, K., Mawan, N., Yimyan, N., Sanjunthong, W., Khongdee, P. and Wicharuck, S. 2022. Closing yield gap of maize in Southeast Asia by intercropping systems: A review. **Australian Journal of Crop Science** 16(11): 1224–1233.
- Langmuir, I. 1918. The adsorption of gases on plane surfaces of glass, mica and platinum. **Journal of the American Chemical Society** 40(9): 1361–1403.
- Lonappan, L., Rouissi, T., Das, R.K., Brar, S.K., Ramirez, A.A., Verma, M., Surampalli, R.Y. and Valero, J.R. 2016. Adsorption of methylene blue on biochar microparticles derived from different waste materials. **Waste Management** 49: 537–544.
- Malik, S. and Laura, J.S. 2025. Evaluating biochar properties derived from various agro-residues via pyrolysis: A comparative study. **Oriental Journal of Chemistry** 41(1): 120–126.
- Mei, Y., Zhuang, S. and Wang, J. 2025. Adsorption of heavy metals by biochar in aqueous solution: A review. **Science of the Total Environment** 968: 178898.
- Office of Agricultural Economics. 2023. **Agricultural statistics of Thailand report**. Ministry of Agriculture and Cooperatives, Bangkok. (in Thai)
- Omara, P., Singh, H., Singh, K., Sharma, L., Otim, F. and Obia, A. 2023. Short-term effect of field application of biochar on cation exchange capacity, pH, and electrical conductivity of sandy and clay loam temperate soils. **Technology in Agronomy** 3: 16.
- Pandian, K., Vijayakumar, S., Mustaffa, M.R.A.F., Subramanian, P. and Chitraputhirapillai, S. 2024. Biochar: A sustainable soil conditioner for improving soil health, crop production and environment under changing climate: A review. **Frontiers in Soil Science** 4: 1376159.
- Phadtare, P.D. and Kalbande, S.R. 2022. Biochar production technologies from agricultural waste, its utilization in agriculture and current global biochar market: A comprehensive review. **International Journal of Environment and Climate Change** 12(11): 1010–1031.
- Tran, H.N., You, S.J., Hosseini-Bandegharai, A. and Chao, H.P. 2017. Mistakes and inconsistencies regarding adsorption of contaminants from aqueous solutions: A critical review. **Water Research** 120: 88–116.
- Udawatta, M.M., Silva, R.C.L.D. and Silva, D.S.M.D. 2023. Surface modification of *Trema orientalis* wood biochar using natural coconut vinegar and its potential to remove aqueous calcium ions: Column and batch studies. **Environmental Engineering Research** 28(1): 210522.
- Wdowiak, A., Podgórska, A. and Szal, B. 2024. Calcium in plants: An important element of cell physiology and structure, signaling, and stress responses. **Acta Physiologiae Plantarum** 46: 108.
- Zeng, S. and Kan, E. 2022. Sustainable use of $\text{Ca}(\text{OH})_2$ modified biochar for phosphorus recovery and tetracycline removal from water. **Science of the Total Environment** 839: 156159.